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[Contributions from the Sheffield Laboratory of Yale University.]

ON THE MOLECULAR CONDITION OF SALTS DISSOLVED IN A FUSED SALT. II. THE ELECTRICAL CONDUCTIVITY OF SALTS IN FUSED MERCURIC CHLORIDE.

BY H. W. FOOTE AND N. A. MARTIN.

In a previous article[1] it has been shown that a salt dissolved in a fused salt may be largely dissociated although its molecular weight, as shown by the freezing point method, is normal, provided the salt which acts as solvent is also largely dissociated. Thus, sodium chloride dissolved in sodium chlorate exhibits a normal molecular weight by the freezing point method, but if the chlorate is largely dissociated, as is indicated by its high conductivity, then sodium chloride may also be dissociated since its sodium ions would repress the dissociation of the chlorate and the effect, on the freezing point, of the two ions added would be the same as that of a single molecule.

The case is different, however, if the solvent salt is a nonconductor and therefore undissociated. In that case, if a salt such as sodium chloride were dissolved and dissociated,

[1] Foote and Levy: THIS JOURNAL, 37, 494.

its ions could not repress the dissociation of the solvent and the lowering in the freezing point, if the salt were completely dissociated, would be twice as great as the lowering if there were no dissociation. In other words, if a salt dissolves in a nonconducting fused solvent and exhibits a high conductivity, molecular weight determinations would be expected to give values much lower than the calculated ones. The case is similar to that of a salt dissolved in water.

Recently the molecular weights of the alkali chlorides and of mercurous and cuprous chlorides in fused mercuric chloride have been determined by Beckmann by means of the depression of the freezing point.[1] The molecular weights found agree very closely indeed with those calculated in every case except that of cuprous chloride, in which the values found lie between the values for CuCl and Cu_2Cl_2. The molecular weight of mercurous chloride corresponded closely to Hg_2Cl_2.

We found in preliminary experiments that fused mercuric chloride is a very poor conductor of the current but that the conductivity is very largely increased by the addition of a small amount of an alkali chloride. The case seemed interesting enough to warrant investigation and we have carried out a considerable number of conductivity determinations and shall attempt an explanation of the results.

The electrodes used in determining the conductivity are shown in Fig. I. The electrode at the left was fastened firmly by a screw in the cover, which was made of brass. The other electrode was passed through an opening in the cover, and was bent as represented and fastened securely in a porcelain tube to insulate it from the other electrode. The porcelain tube was held in the cover by a screw as shown. The ring in the cover was used in lifting the electrodes. We had some difficulty at first in fastening the electrode wire firmly in the porcelain tube. We succeeded best by roughening the platinum wire, then igniting it in the tube with a strong solution of water glass. Quartz tubes covered part of the wires as shown in the diagram. At first we used a lead glass coating which was fused on, but this was unsatisfactory. It appar-

[1] Z. anorg. Chem., **55**, 175.

ently conducted the current at a high temperature. The electrodes were made entirely of platinum and the wire was heavy enough so that it did not bend. The capacity of the vessel was determined in the ordinary manner with a standard potassium chloride solution.

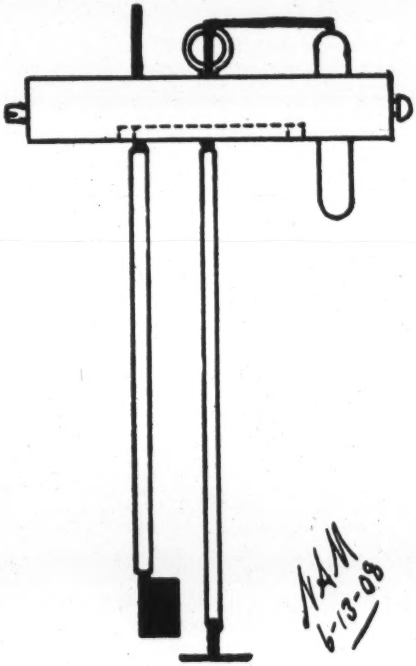


Fig. I.

The conductivity measurements were made by the customary Kohlrausch method at 282°. Several kilograms of a fusible mixture containing about equal parts of potassium

and sodium nitrates and sodium nitrite were used as a bath to keep the salts in the conductivity vessel fused at a constant temperature. The temperature of the bath varied by about one degree during the measurements.

The melting and boiling points of mercuric chloride lie very near together so that when fused, the salt volatilized rapidly, and in a series of determinations a correction in the amount of mercuric chloride had to be applied on account of loss by volatilization. The loss proceeded at a nearly uniform rate and an empirical correction was made. The density of fused mercuric chloride was found to be 4.36 at 282° and the volume of all solutions was calculated from the weight of mercuric chloride and this value for the density.

The specific conductivity of the ordinary C. P. mercuric chloride was found in one determination to be 2.5×10^{-4}. After recrystallizing, it became in one case 5.8×10^{-5}. All the recrystallized samples had a specific conductivity of the same order. All measurements were made with mercuric chloride which had been recrystallized one or more times. The specific conductivity of the mercuric chloride used in each case was deducted from the specific conductivity of the solution in order to calculate the molecular conductivities.

As the solutions could not conveniently be prepared at any particular concentration, the results calculated from two series of determinations were plotted and the conductivities at the dilutions shown in the table were read directly from the curves. The results were as follows:

Molecular Conductivity of Alkali Chlorides and Cuprous Chloride in Fused Mercuric Chloride at 282°.

V (liters).	CsCl.	KCl.	NH_4Cl.	NaCl.	CuCl.
2	....	81.0	....	61.5	70.0
4	....	66.5	70.0	47.0	46.0
5	70.0	62.0	64.5	43.0	42.0
8	60.5	54.0	55.2	34.0	34.0
10	57.0	50.5	52.0	31.3	31.2
15	51.0	45.7	46.5	28.0	26.0
20	48.5	43.4	....	....	24.0
25	46.5	40.8	....	....	....
30	44.0	38.5	....	....	....

The curves representing the results graphically for the alkali chlorides are shown in Fig. II. Some of them have been prolonged slightly beyond the points actually determined. It will be noticed that the curves are all similar in type and that conductivity decreases with dilution in every case.

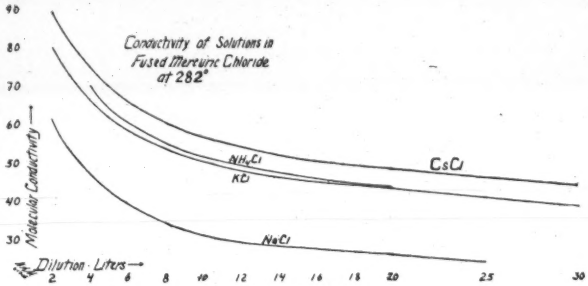


Fig. II.

The facts to be explained are that the chlorides have normal molecular weights as shown by the depression of the freezing point and that they have high molecular conductivity. The most probable explanation seems to be the formation of a complex salt which dissociates in solution:

$$2MCl + HgCl_2 \longrightarrow M_2HgCl_4 \longrightarrow \overset{+}{M} + \overset{-}{M}HgCl_4.$$

On this assumption, two molecules of alkali chloride give two ions, so that the depression due to the ions would be the same as that due to the original salt. The formation of a compound, $MHgCl_3$, appears to be impossible. This salt would form two ions from one molecule of alkali chloride, so in this case the molecular weight would necessarily be lower than the calculated.

Some indirect evidence bearing on the probable formation of the salt M_2HgCl_4 was obtained. A corresponding salt of a bivalent element, $MHgCl_4$, could not dissociate in the same manner. We attempted to prepare solutions containing the

chlorides of bivalent elements in order to measure their conductivity and were surprised to find they were nearly all insoluble. Thus barium chloride was insoluble although the presence of mercuric chloride increases its solubility in water enormously. The only chloride of a bivalent element which we found to be soluble was cupric chloride, which was slightly soluble, giving a distinct brown color to the solution. The conductivity of mercuric chloride was not, however, perceptibly changed by the presence of the cupric chloride. Anhydrous ferric chloride and mercurous chloride are also soluble in mercuric chloride but their solutions, too, are nonconductors. The readiness with which the alkali chlorides dissolve, on the other hand, is very striking. It appears then that alkali chlorides which can dissociate according to the equation $M_2HgCl_4 \longrightarrow M + MHgCl_4$ are very readily soluble while if the salt is of such a type that it cannot dissociate in this way, it either does not dissolve or else, if dissolved, it does not conduct the current.

If the complex M_2HgCl_4 is formed, it must be practically all dissociated, for if it were not, two molecules of alkali chloride would yield one molecule of complex salt, and molecular weight determinations would give high results.

The dissociation according to the expression

$$2NaCl + HgCl_2 \longrightarrow \overset{+}{Na} + \overset{-}{NaHgCl_4}$$

is independent of the dilution, as the number of ions is equal to the number of molecules of sodium chloride. The molecular conductivity in this case should not change with the concentration. The results, however, show gradual increase of conductivity with the concentration until the more concentrated solutions are reached, when the conductivity rises rapidly. This is very likely due to the formation of increasing amounts of some other complex salt in solution, the amount being small at first but increasing in the more concentrated solutions. Thus the salt M_3HgCl_5 may be formed, dissociating into $\overset{+}{M} + \overset{+}{M} + \overset{=}{MCl_5}$. This would not affect the molecular weight but would change the conductivity.

Whether all the dissolved alkali chloride is converted into a complex salt or not we have no certain means of determining, but the fact that nearly all salts of a diacid base, like barium, are insoluble, while the alkalies are exceedingly soluble, makes it very probable that the solubility is due to the formation of the dissociated complex salt and that the action is nearly or quite complete.

The difference in the behavior of cuprous and mercurous chlorides is noticeable, solutions of mercurous chloride not being conductors while solutions of cuprous chloride conduct readily. Beckmann found the molecular weight of mercurous chloride corresponded to Hg_2Cl_2 and that of cuprous chloride to a mixture of CuCl and Cu_2Cl_2. Apparently the double molecules do not form dissociated complex molecules with the solvent while the single molecules of cuprous chloride behave like sodium chloride, forming the dissociated double salt.

NEW HAVEN, CONN.,
April, 1909.

STUDIES IN CATALYSIS:

ON THE FORMATION OF ESTERS FROM AMIDES AND ALCOHOLS.

[TENTH COMMUNICATION ON CATALYSIS.]

BY S. F. ACREE.

(We are indebted to the Carnegie Institution of Washington for aid in our work on catalysis.)

Esters, amides, cane sugar, oximes, etc., are hydrolyzed far more rapidly in aqueous solutions when in the presence of strong mineral acids than when such acids are absent, and this catalysis is now generally explained on the assumption of the formation of intermediate compounds by the union of the acid catalyzer and the ester, sugar, etc.

Kastle,[1] Euler,[2] Acree,[3] Bredig,[4] Lapworth,[5] Stieglitz,[6] and Goldschmidt[7] have all contributed researches which, as a whole, showed that the ideas involved in using the theory of ionization in acid catalysis, together with the assumption of intermediate salts or double compounds, are most probably the correct ones when it is postulated that the cation of the ester salt is hydrolyzed. In 1904–'05 Acree and Brunel[8] proposed the theory and began experimental work to prove that in the *alkaline catalysis* of the formation of esters from acids and alkyl halides the *anion* of the salt is the substance transfromed, and Acree and Johnson predicted the same of the hdyrolysis of esters and amides. The close analogy of the theory of acid catalysis to Acree's theory of alkaline[9] catalysis can be seen at a glance from the following table:

[1] See P. Am. Assn. Adv. Sci., **47**, 238, for an abstract of the original article, which was never published in full, and which Prof. Kastle kindly sent me at my request.

[2] Z. physik. Chem., **36**, 405, 663; **40**, 501; **47**, 356; Z. physiol. Chem., **52**, 146.

[3] Acree and Hinkins: THIS JOURNAL, **28**, 370. This work was entirely completed in the spring of 1901. I believe that the mechanism of the reactions assumed in this paper is wrong and have adopted the view first presented by Kastle and Bredig. See R. F. Brunel's dissertation, Johns Hopkins, 1906, begun in 1904–5; J. Am. Chem. Soc., **30**, 1755; THIS JOURNAL, **37**, 71, 410; **38**, 258, 489, 746; **39**, 145, 226, 300; and especially, **38**, 342, 343, for my views on the mechanism of reactions. Euler has changed his views on the mechanism of catalytic reactions (Z. physiol. Chem., **52**, 146).

[4] Z. Elek. Chem., **9**, 118; **10**, 586; **11**, 528; Ergebnisse der Physiologie, Vol. I., p. 134 (1903); Biochem. Z., **6**, 283; Ber. d. chem. Ges., **41**, 740, 752; and many other articles.

[5] Mellor's Statics and Dynamics, p. 289. See especially J. Chem. Soc., **93**, 30, 85; Chem. News, **97**, 248, 309.

[6] Congress of Arts and Sciences, St. Louis, 1904, **4**, 276; THIS JOURNAL, **31**, 458; **39**, 29, 166, 402, 437, 586, 719.

[7] Ber. d. chem. Ges., **29**, 1369, 1899; **32**, 3390; **39**, 97, 109, 711; Z. physik. Chem., **56**, 1, 385; and many other papers.

[8] Brunel's Dissertation, Johns Hopkins University, 1906.

[9] For a fuller mathematical discussion of the theory of the formation and decomposition of the complex cations and anions see THIS JOURNAL, **37**, 71, 410; **38**, 258, 489; **39**, 124; Ber. d. chem. Ges., **41**, 3199. Dr. Reid now has evidence that the catalysis of amides by alkalies may not be exactly like saponification.

$$\left.\begin{matrix}CH_3CONH_2 + H_2O \longrightarrow CH_3\overset{+}{C}ONH_3 + \overset{-}{O}H \\ \text{Weak base} \qquad\qquad \text{few cations}\end{matrix}\right\} + H_2O \longrightarrow \underset{\text{few complex cations}}{CH_3C(OH)_2\overset{+}{N}H_3} + \overset{-}{O}H \longrightarrow \underset{\text{slow reaction}}{CH_3COOH} + NH_4OH$$

$$\left.\begin{matrix}CH_3CONH_2 + HCl + H_2O \longrightarrow CH_3\overset{+}{C}ONH_3 + \overset{-}{C}l \\ \qquad\qquad\qquad\qquad \text{many cations}\end{matrix}\right\} + H_2O \longrightarrow \underset{\text{many complex cations}}{CH_3C(OH)_2\overset{+}{N}H_3} + \overset{-}{C}l \longrightarrow \underset{\text{fast reaction}}{CH_3COOH} + NH_4Cl$$

$$\left.\begin{matrix}UrH + C_2H_5I \longrightarrow \overset{-}{U}r + \overset{+}{H} + C_2H_5I \\ \text{Weak acid} \qquad\qquad \text{few anions}\end{matrix}\right\} \longrightarrow \underset{\text{few complex anions}}{\overset{-}{U}r.IC_2H_5} + \overset{+}{H} \longrightarrow \underset{\text{slow reaction}}{UrC_2H_5} + \overset{+}{H} + \overset{-}{I}$$

$$\left.\begin{matrix}UrH + NaOH \longrightarrow \overset{-}{U}r + \overset{+}{N}a + C_2H_5I \\ \qquad\qquad\qquad\qquad \text{many anions}\end{matrix}\right\} \longrightarrow \underset{\text{many complex anions}}{\overset{-}{U}r.C_2H_5I + \overset{+}{N}a} \longrightarrow \underset{\text{fast reaction}}{\overset{+}{U}rC_2H_5} + \overset{+}{N}a + \overset{-}{I}$$

$$\left.\begin{matrix}CH_3COOR + \overset{+}{H} + \overset{-}{O}H \longrightarrow CH_3C(OH)(OR)(\overset{-}{O}) + \overset{+}{H} \\ \text{Weak acid in water} \qquad\qquad \text{few complex anions}\end{matrix}\right\} \longrightarrow \underset{\text{slow reaction}}{CH_3COOH} + ROH$$

$$\left.\begin{matrix}CH_3COOR + H_2O + \overset{+}{N}a + \overset{-}{O}H \longrightarrow CH_3C(OH)(OR)(\overset{-}{O}) + \overset{+}{N}a \\ \qquad\qquad\qquad\qquad\qquad\qquad \text{many complex anions}\end{matrix}\right\} \longrightarrow \underset{\text{fast reaction}}{CH_3\overset{-}{C}OO + \overset{+}{N}a} + ROH$$

In 1907, Acree,[1] Johnson, and Nirdlinger furnished quantitative evidence that the hydrazide, amide, and oxime cations are hydrolyzed,

$$(CH_3)_2C{=}NOH + \overset{+}{H} + \overset{-}{Cl} + H_2O \rightleftarrows$$

$$(CH_3)_2C{=}\overset{+}{N}HOH + \overset{-}{Cl} + H_2O \rightleftarrows$$

$$(CH_3)_2C\begin{matrix}\diagup OH \\ \diagdown \overset{+}{N}H_2OH\end{matrix} + \overset{-}{Cl} \rightleftarrows (CH_3)_2CO + \overset{+}{N}H_3OH + \overset{-}{Cl},$$

and in 1908 Stieglitz[1] and his coworkers published a number of brilliant researches on the imidoesters which had been under way since 1898. Pinner had shown more than 16 years before that the imidoester salt is hydrolyzed and Stieglitz proved conclusively that the imidoester cation is catalyzed.

In connection with the above theory of intermediate compounds it should be mentioned that Bredig[1] and his coworkers have studied the catalytic action of cyanide ions in benzoin formation, of hydrogen ions in the decomposition of diazoacetic ester, of iodide ions on the change of hydrogen peroxide, etc. Lapworth[1] studied the catalytic action of hydrogen ions on the bromination of ketones, on esterification and saponification, and on oxime formation. Goldschmidt[1] has investigated the catalytic action of acids on esterification, reduction and oxidation phenomena, etc., and Kastle[2] the catalytic action of enzymes on ester formation and decomposition, the action of acids in the bromination of phenols, formation of esters, etc. It is evident then that in the last decade a large number of workers have been studying catalysis from the same general point of view and the future bids fair to clear up a large number of the very important problems of this field. Catalysis is regarded as only a part of the broad domain of *the study of the mechanism of reactions*, all of which must be investigated from the same general point of view.

[1] *Loc. cit.*

[2] P. Am. Assn. Adv. Sci., **47**, 238; THIS JOURNAL, **24**, 491; **26**, 518; **29**, 397, 563; **31**, 521; **32**, 376.

ON THE REARRANGEMENT OF ACETYLHALOGENAMINOBENZENE DERIVATIVES.

Acree and Johnson published a very full[1] account of all the researches on catalysis which had appeared up to 1907, and developed fully the correct equations for treating mathematically the theory of intermediate compounds, this having been done only incompletely by Bredig, Lapworth, Stieglitz, Goldschmidt, etc. These equations show that two of the three old so-called laws of catalysis can not possibly hold in all catalytic reactions, these laws being merely "approximate expressions of special reactions," such as the inversion of cane sugar, reversible ester formation, and hydrolysis of amides. The second and third so-called laws of catalysis, which postulated that "the catalyzer affects the velocity constant directly in proportion to the concentration of the catalyzer" and that "a change in the concentration of the catalyzer does not change the equilibrium point in reversible reactions," were developed under the assumption that the catalyzer does not take part in the reaction. But from the newer point of view we look upon a catalyzer as a substance which accelerates (or suppresses)[2] a reaction chemically because it forms an intermediate addition product which is more (or less) reactive than the original noncatalyzed reacting substances. From this point of view there is no sharp dividing line between the old so-called cases of pure catalysis, such as the hydrolysis of cane sugar, esters, etc., in which the amount of salt formed is very small, and those cases in which the amount of salt or double compound present is very large and which cannot be called catalysis at all in the old sense. On this assumption it was developed mathematically that there are many conditions under which these two laws can hold, and others under which they cannot hold, whether there are only traces or much of the intermediate

[1] Bredig and also Lapworth have referred to this article as a general summary of the facts of importance to catalysis (Ber. d. chem. Ges., **41**, 754, 755; J. Chem. Soc., **93**, 2163).

[2] This does not necessarily include the catalytic effect of solvents in changing eaction velocities because of change in viscosity, vapor tension, heat of dilution, and unknown factors which influence reactions.

compound formed. For instance, it was shown experimentally by Blanksma[1] and more fully by Acree and Johnson[2] that hydrochloric acid causes a catalysis of acetylbrom(chlor)-aminobenzene into *p*-brom(chlor)acetanilide in proportion to the square of the concentration of the hydrochloric acid instead of the first power of this concentration as demanded by the above second law of catalysis. The simplest[3] explanation of this is that the acetylbrom(chlor) aminobenzene unites not only with the hydrogen ion but also with the chloride ion, present in the same concentration, which therefore acts as a *cocatalyzer*[4] with the hydrogen ion. This view is supported by a large number of other facts, such as the following: the reaction velocity of acetylchloraminobenzene in acetic acid, or in a mixture of acetic acid and hydrochloric acid, is increased by the addition of potassium chloride (and hence chloride ions) because the increase in the concentra-

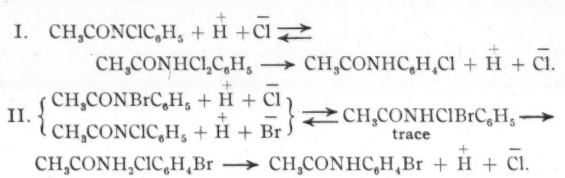
[1] Rec. trav. chim., **21,** 366; **22,** 290.

[2] This Journal, **37,** 410; **38,** 265.

[3] Some other explanations, based partly on other mechanisms of the action of the hydrogen or halide ion as a cocatalyzer, have suggested themselves. These will be treated experimentally but do not seem probable at present. The cation may be also undergoing transformation with a much smaller velocity. The explanation proposed by Cohen and Cross (P. Chem. Soc., **23,** 148; This Journal, **39,** 431) is certainly not complete (see *loc. cit.* and This Journal, **38,** 746; **39,** 544).

[4] The bromide, acetate, sulphate, etc., ions can be used instead of the chloride ions as a cocatalyzer in this reaction: *i. e.*, acetylbromaminobenzene is changed into *p*-bromacetanilide by various acids. But in this reaction the bromide ion is at least 1000 times as active as the chloride ion as a cocatalyzer, and acetate and sulphate ions are far less active than the chloride ion. Likewise acetylchloraminobenzene is changed into *p*-chloracetanilide by hydrochloric acid very smoothly at 4°, while hydrobromic acid causes a corresponding change of this chloramide derivative into the *p*-bromacetanilide at 3° at least 100 times as rapidly. These facts therefore give further light on the possible action of co-enzymes because the mechanism of our reaction is clear and recalls certain very interesting co-enzyme reactions. Pepsin seems to be practically inactive unless hydrogen ions are present, and trypsin does not react in the absence of hydroxyl ions. Asparagine seems to act as a specific co-enzyme with amylase, and zymase seems to have two enzymes which act together, either alone being inactive (See Bayliss: "The Nature of Enzyme Action," p. 65). The reactions of these substances, as well as those of the anti-toxins, may all depend entirely upon the velocity of formation and change of the intermediate *catalyzer.cocatalyzer.substrate* double compounds. But we must distinguish in all cases between the laws for true solutions and those for colloidal solutions or suspensions, a fact too often overlooked. The fact that these two cocatalyzers, the bromide ion and the chloride ion, are about as closely related chemically as any substances that we have, and yet have such greatly different catalytic effects in the above reactions, may be of great importance in a large number of phenomena of biological chemistry; two apparently related substances, ions or enzymes, may sometimes have widely different actions in the plant and animal world.

tion of the chloride ions causes an increase in the concentration of the undissociated salt, as demanded by the equations below. The concentration of this undissociated acetylbrom-(chlor)aminobenzene salt, which is the substance undergoing transformation, is roughly proportional to the square of the concentration of the hydrochloric acid when the acid is nearly completely ionized.



Now the data of Blanksma, and those of Acree and Johnson obtained in the preliminary study of the catalytic action of hydrochloric acid on acetylchloraminobenzene, show roughly that this formulation is probably correct. The uncertainty in the calculations for the rather concentrated solutions necessary for the study of the reaction, together with the large analytical error, make exact calculations of no value. The data obtained show roughly, however, that the reaction velocity is proportional to the *square* of the concentration of the hydrochloric acid, which is represented in terms of M = 10 cc. of 28.67 per cent hydrochloric acid in 500 cc. of 30 per cent acetic acid solution. The values for K are those obtained in 30 per cent acetic acid solution.

	K.	0.5 M.	M.	1.5 M.	2 M.	2.5 M.	3 M.	5 M.
Found	0.00103	0.0036	0.0087	0.0146	0.0239	0.0313	0.113	
Calc.	0.00098	0.0039	0.0087	0.0154	0.0242	0.0348	0.097	

In the study of the action of hydrobromic acid on acetylchloraminobenzene in 10 per cent acetic acid at 3°, however, the reaction was found to proceed so rapidly in even dilute solutions of hydrobromic acid that much more exact data could be obtained. We have therefore now calculated the constants by making the proper corrections for the suppres-

sion of the ionization of the acetic acid by the hydrobromic and hydrochloric acids, taking $K = 0.000018$ at 3° and considering the ionization of the hydrobromic and hydrochloric acids to be the same in the acetic acid solution as it is in water, both of which assumptions are not far from right.

The application of the mass law to reactions II. above gives us the approximate equation,

$$\frac{dx}{dt} = K(C_a - x)(C_{Br} - x)C_H \text{ or } KC_HC_{Br} = \frac{x}{t(A - x)},$$

in which the proper concentrations, in gram molecules per liter, of hydrogen ions, C_H, bromide ions, C_{Br}, and acetylchloraminobenzene, C_a, must be substituted. When this is done the following rounded values are obtained:

Table.	C_a.	C_{HBr}.	C_{Br}.	C_H.	$KC_{Br}C_H$.	K.
I.	0.0024	0.0024	0.00232	0.00676	0.0111	710
II.	0.0040	0.0040	0.00390	0.00770	0.0210	700
III.	0.00586	0.00586	0.00565	0.0090	0.0388	760
IV.	0.0078	0.0078	0.00746	0.01033	0.0568	740
V.	0.01134	0.01134	0.01070	0.0130	0.1000	720
VI.	0.01714	0.01714	0.01595	0.0176	0.2050	730
VII.	0.0210	0.0210	0.0194	0.0244	0.345	730
					Average.....	730

The values for K give what we must call a very good consant when we consider the difficult experimental conditions, especially the fact that light affects the reaction velocity so greatly. We are justified then in making a further study of this problem from this point of view.

Another problem which we developed theoretically and proved experimentally was that the third law of catalysis cannot hold in some cases, whether the concentration of the intermediate compound be large or small, and yet may hold approximately in other reactions. To illustrate with one of many possible examples, it was seen that if in a reversible reaction we have a base in each of the opposing sets of reacting substances, and if the reaction is catalyzed

by acids because of the formation of more reactive salts of the bases, then the equilibrium point of the reaction must be altered by a change in the amount of acid added if the two bases have not the same affinity constants. We chose the reversible formation of oximes to test this principle, and Johnson's experimental work, and also that of Lapworth[1] and his coworkers, proved beyond question that our ideas are correct.

$$(CH_3)_2CO + NH_2OH \rightleftarrows (CH_3)_2C = NOH + H_2O.$$

$$(CH_3)_2CO + \overset{+}{N}H_3OH + \bar{C}l \rightleftarrows$$

$$(CH_3)_2C(OH)\overset{+}{N}H_2OH + \bar{C}l \rightleftarrows$$

$$(CH_3)_2C = \overset{+}{N}HOH + H_2O + \bar{C}l \rightleftarrows$$

$$(CH_3)_2C = NOH + \overset{+}{H} + \bar{C}l + H_2O,$$

or

$$(CH_3)_2CO + NH_2OH + \overset{+}{H} + \bar{C}l \rightleftarrows$$

$$(CH_3)_2CO.\overset{+}{H} + NH_2OH + \bar{C}l \rightleftarrows$$

$$(CH_3)_2C(OH)\overset{+}{N}H_2OH + \bar{C}l \rightleftarrows$$

$$(CH_3)_2C = \overset{+}{N}HOH + H_2O + \bar{C}l \rightleftarrows$$

$$(CH_3)_2C = NOH + \overset{+}{H} + \bar{C}l + H_2O.$$

Of course, the same line of reasoning can be extended to include the formation of many other intermediate compounds by the action of alkalies, salts, enzymes, organic substances, etc. Professor Bredig has kindly called my attention to the fact that he too has pointed out in the *Ergebnisse der Physiologie*,[2] before our article appeared, that the second and third laws do not always hold. Abel,[3] Euler,[4] and Stieglitz[5] have all recently discussed the same question, and in view of Acree and Johnson's mathematical and experimental proof these

[1] J. Chem. Soc., **91**, 1133.
[2] Vol. I., p. 134.
[3] Z. Elek. Chem., **13**, 555.
[4] Z. physiol. Chem., **52**, 146.
[5] *Loc. cit.*

three old so-called laws of catalysis may be said to be abandoned as a rigid basis for work.

Especially was it developed by Acree and Johnson that reactions may be the result of several independent simultaneous or side reactions, involving both the dissociated and undissociated salts, the free bases or acids, etc., and this point of view should guide all quantitative work. It was shown clearly by our work, and that of Lapworth, on the oximes that at least two and perhaps three reactions may, under certain conditions, be taking place side by side. Mr. Desha is continuing the work on the oximes. We wish our colleagues to leave to us for some time the study of the formation of the amidoximes from the hydroxylamines and amidine salts, and of the hydroxamic acid derivatives. The study of the formation, hydrolysis, and other reactions of these substances should throw important light on the theory of catalytic processes.

ON THE HYDROLYSIS AND ESTERIFICATION OF AMIDES.

Acree and Nirdlinger[1] showed experimentally in a preliminary study that the hydrolysis of amides may be explained on the assumption of the hydrolysis of amide cations,

$$CH_3CONH_2 + \overset{+}{H} + \overset{-}{Cl} + H_2O \longrightarrow$$

$$CH_3\overset{+}{C}ONH_3 + \overset{-}{Cl} + H_2O \longrightarrow CH_3COOH + \overset{+}{NH_4} + \overset{-}{Cl},$$

and it was pointed out that the work of Ostwald,[2] Remsen and Reid,[3] and Crocker,[4] which was undertaken from quite another aspect, harmonized with our point of view. I have had the good fortune now, through the aid of a grant from the Carnegie Institute of Washington, to have this work taken up again by Dr. E. E. Reid to extend his own former work and to give light on our theory. He is studying the hydrolysis and alcoholysis of amides by acids and alkalies, as he reports in the succeeding article.

[1] THIS JOURNAL, **38**, 489.
[2] J. prakt. Chem., **135**, 1.
[3] THIS JOURNAL, **21**, 281; Reid: *Ibid.*, **24**, 397.
[4] J. Chem. Soc., **91**, 593.

I predicted that amides, anilides, hydrazides, etc., would yield esters in alcoholic hydrochloric acid, according to one or both of the following reactions,[1] more probably the first one:

$$\left.\begin{aligned} CH_3CONH_2 + \overset{+}{H} + \overset{-}{Cl} &\longrightarrow CH_3C\overset{+}{O}NH_3 + \overset{-}{Cl} + ROH \\ CH_3CONH_2 + \overset{+}{H} + \overset{-}{Cl} &\longrightarrow CH_3CONH_2 + \overset{-}{Cl} + ROH.\overset{+}{H} \end{aligned}\right\} \longrightarrow$$

$$CH_3C(OH)(OR)\overset{+}{N}H_3 + \overset{-}{Cl} \longrightarrow CH_3COOR + \overset{+}{N}H_4 + \overset{-}{Cl}.$$

Dr. Reid also saw this problem independently and has since found that amides give practically quantitative yields of esters. Messrs. Bransky and Chazal have also found that benzphenylhydrazide and benzanilide give excellent yields of ethyl benzoate. The study of the esterification of amides, anilides, hydrazides, etc., is of especial interest from several points of view. The reactions are exactly analogous, on the one hand, to those of the hydrolysis of esters and amides, and, on the other hand, to those of the esterification of organic acids, which have been the subject of detailed study in recent years by Goldschmidt[2] especially, and by Lapworth,[3] Weg-

[1] Although the formation of an imidoester by the alternate reaction,

$$CH_3C(OH)(OR)\overset{+}{N}H_3 \longrightarrow CH_3C(OR) = \overset{+}{N}H_3 + H_2O,$$

and the formation of an ester or ortho-ester from the imidoester salt,

$$CH_3C(OR) = \overset{+}{N}H_3 + H_2O \longrightarrow CH_3COOR + \overset{+}{N}H_4$$

$$CH_3C(OR) = \overset{+}{N}H_3 + 2ROH \longrightarrow CH_3C(OR)_3 + \overset{+}{N}H_4,$$

have never been observed, and the constants of the reactions indicate that these cannot be present in large quantity, yet this may be found to be true in other cases in later studies. Dr. Reid has found that the *m*-nitrobenzamide gives a quantitative yield of the ethyl *m*-nitrobenzoate. There seems to be a general tendency in acid and alkaline catalysis for the catalyzed substance, itself an acid or base, to go over into the salt of a stronger acid or base when the reaction goes nearly or quite to completion. Acree and Johnson found, however, that in reversible oxime formation the stronger base, hydroxylamine, goes partly into a weaker base, acetoxime. It is easy to show that *in all cases* the reactions take place because of a decrease in the free energy of the system as demanded by the second law of thermodynamics. This point of view has been insisted upon and used most brilliantly for years by Michael, for the organic chemists, and by Euler, Plank, Nernst, Abegg, and many other physical chemists. A brilliant field for investigation in organic chemistry is the study of changes in free and total energy of reacting systems by the use of electromotive force measurements, calorimetric data of many kinds, etc. We propose to study the reactions of hydroxylamines, alcohols anilines, semicarbazides, etc., with the salts of amides and other similar compounds.

[2] Ber. d. chem. Ges., **39**, 711; Z. physik. Chem., **60**, 728.

[3] *Loc. cit.* and also J. Chem. Soc., **93**, 2163, 2187; P. Chem. Soc., **24**, 101, 152.

scheider[1] and Kailan, Julius Meyer,[2] Rosanoff,[3] Michael,[4] etc. New evidence obtained by work on the amides should throw light on the entire subject of catalysis. There is, furthermore, a great advantage in working with these nitrogen compounds in that they are stronger bases than the organic esters or acids and hence the concentration of the salt[5] formed can be measured more easily, although the amount of this salt is so small that these reactions might still be looked upon as belonging to the old field of so-called pure catalysis. Another great advantage can be seen from the following: In studying the rates of formation of esters from organic acids and alcohols, Goldschmidt especially, and also Bredig and Fraenkel,[6] Kailan,[7] and Gyr[8] recently, have observed that even small amounts of water affect the reaction velocity very greatly, and render interpretations of the reactions uncertain. It is absolutely impossible to eliminate this disturbing factor in the esterification work because water is formed in the reaction:

$$CH_3COOH + ROH \rightleftarrows CH_3COOR + H_2O.$$

But no appreciable amount of water is formed in the esterification of amides and hence a very great disturbing factor is eliminated. The absence of this factor not only shows itself in the concordance of Dr. Reid's velocity constants, but also renders possible much more accurate work in the determination of the conductivities, concentrations, or hydrolysis, of the reacting salts, and of change in viscosity, vapor tension, heat of dilution, etc., of the solutions.

But a very great reason for studying the esterification of

[1] Sitzun. Wien., **116**, II., 55; Ber. d. chem. Ges., **39**, 1055; Ann. Chem. (Liebig), **351**, 186.

[2] Z. Elek. Chem., **13**, 186, 485, 494; Z. physiol Chem., **66**, 81.

[3] J. Am. Chem. Soc., **30**, 1895, 1908.

[4] Ber. d. chem. Ges., **42**, 310, 317.

[5] Acree and Johnson found that a number of organic esters and other carbonyl compounds lower the conductivity of alcoholic and aqueous hydrochloric acid a very slight amount, probably due to the formation of ester salts. Goldschmidt failed to detect any such salt formation by ethyl phenylacetate. Acree and Nirdlinger: THIS JOURNAL, **38**, 489.

[6] Biochem. Z., **6**, 308.

[7] *Loc. cit.*; Monatsh. Chem., **28**, 559, 571, etc.

[8] Ber. d. chem. Ges., **41**, 4322.

the amides was the desire to secure light on certain phases which have come out not only in our own work but also in Goldschmidt's theory of the formation of esters from organic acids and alcohols in the presence of strong acids. This brilliant worker in the field of quantitative organic chemistry has proposed, as an alternative to the generally accepted views, the theory that the hydrogen ions of a catalyzing acid unite with the alcohol and that this complex cation reacts with the organic acid as follows:

$$CH_3COOH + \overset{+}{H} + \overset{-}{Cl} + ROH \rightleftarrows$$

$$CH_3COOH + ROH.\overset{+}{H} + \overset{-}{Cl} \rightleftarrows$$

$$CH_3C(OH)(OR)(OH.\overset{+}{H}) + \overset{-}{Cl} \rightleftarrows$$

$$CH_3COOR + H_2O.\overset{+}{H} + \overset{-}{Cl} \rightleftarrows$$

$$CH_3COOR + H_2O + \overset{+}{H} + \overset{-}{Cl}.$$

This theory is analogous to that proposed by A. A. Noyes several years ago to account for catalytic hydrolysis. Goldschmidt has without doubt gone more deeply into the study of esterification than other workers and his views are to be given great respect. Dr. Reid's work seems to me all the more important, therefore, because the study of the esterification of amides would throw light on some questions that cannot be taken up or solved in Goldschmidt's work.

For instance, Goldschmidt cannot easily measure accurately the real amount of the cation formed by the union of the hydrogen ion and the alcohol or organic acid to be esterified. In the work on the amides, however, Acree and Nirdlinger showed by conductivity methods that an amide salt is actually formed, and we shall attempt to measure the basic and acid constants of a large number of such substances as acetamide, benzamide, mono- and dimethylbenzamide, benzhydroxamic acid and its esters, aminoacetic acid and its homologues, the amides and especially half amides of dibasic acids, such as succinic acid, etc. This is a very important question, because if it were possible to measure accurately the real concentrations of the amide salt and of the alcoholated hy-

drogen ions it would obviously be possible to determine whether the decomposing complex cation[1] $CH_3C(OR)(OH)\overset{+}{N}H_3$ (or undissociated salt) is formed by the union of the alcohol and the amide salt or ion, or the union of the alcoholated hydrogen ion with the amide, or both. When the amide is a very weak base the hydrogen ions will divide themselves between the water, alcohol, and amide, but when the amide is a very strong base it will use practically all of the hydrogen ions for salt formation, and there will be no appreciable concentration of hydrated or alcoholated hydrogen ions remaining. Lapworth[2] and Goldschmidt[3] have recently treated this subject extensively mathematically and experimentally. Goldschmidt's theory requires that the addition of water shall lower the esterification constants of all organic acids to about the same extent, and this has been verified experimentally by him. But I predicted that the change in constant would vary with the amide, and Dr. Reid finds variations as large as 50 per cent; much work is needed from all these points of view.

To approach this problem it would obviously be necessary to know the concentrations of the salts as well as to measure the degree of alcoholation and hydration of the hydrogen ion by methods like those of Frazer and Holmes,[4] Noyes and Washburn,[5] and Buchböck.[6] This is entirely analogous to the problem involved in the study of the formation of esters from alkyl halides and salts, which Acree,[7] and later Goldschmidt,[8] supposed takes place through the formation and the decomposition of a complex anion, and which we are studying minutely in this laboratory.

$$C_2H_5I + \overset{+}{A}g + \overset{-}{N}O_3 \rightleftharpoons C_2H_5I.\overset{-}{N}O_3 + \overset{+}{A}g \rightleftharpoons C_2H_5NO_3 + \overset{+}{A}g + \overset{-}{I}.$$

[1] This is given only as the most probable formula: there may be several forms of this salt in equilibrium. Acree and Johnson: THIS JOURNAL, **38**, 337, 341.

[2] J. Chem. Soc., **93**, 2187.

[3] Z. Elek. Chem., **15**, 4.

[4] THIS JOURNAL, **40**, 319.

[5] J. Am. Chem. Soc., **31**, 322.

[6] Z. physik. Chem., **55**, 563.

[7] THIS JOURNAL, **38**, 262; **39**, 244; Ber. d. chem. Ges., **41**, 3214.

[8] Z. Elek. Chem., **14**, 581.

Of course, both of the above reactions of the amides may be taking place side by side, a phase that we are investigating especially, as Lapworth and Acree, Johnson, and Desha have found such to be the case in oxime formation.

In this connection I wish to call attention to the light which Dr. Reid's work sheds on another important phase of this general problem. About seventeen years ago Pinner published in his book, *Die Imidoaether und ihre Derivate*, the results of investigations which showed that the hydrochlorides of imidoesters are not only hydrolyzed into ammonium chloride and the corresponding ester, but that they are also alcoholyzed or esterified into ammonium chloride and the corresponding ortho esters, these two reactions being therefore entirely analogous.

$$ROCH = NH_2Cl + H_2O \longrightarrow ROCHO + NH_4Cl$$
$$ROCH = NH_2Cl + 2ROH \longrightarrow ROCH(OR)_2 + NH_4Cl$$

Claisen[1] has used this reaction for the preparation of nascent ortho esters in the presence of ketones in order to obtain ketals, and recently Reiter and Hess[2] have taken up this study again. Stieglitz[3] has proposed a theory to explain this reaction based on the assumption of the formation and reactions of an olefine compound, such as $CH = C(OC_2H_5)_2$. He states (note 3, page 721) that the "*difference* (italics mine) in the result of this action and that of water on such salts" suggested the following reactions:

$$CH_3C(=\overset{+}{N}H_2)OC_2H_5 + HOC_2H_5 \longrightarrow$$
$$CH_3C(\overset{+}{N}H_3)(OC_2H_5)_2 \longrightarrow CH_2=C(OC_2H_5)_2 + \overset{+}{N}H_4$$
and $$CH_2 = C(OC_2H_5)_2 + HOC_2H_5 \longrightarrow CH_3C(OC_2H_5)_3;$$

and he found further evidence for this point of view in the fact that in the case of cyanacetic ester an olefine compound, $ROOCCH = C(OC_2H_5)_2$, was actually obtained as an intermediate or final product, while benzimidoesters apparently did not yield such ortho esters.

[1] Ber. d. chem. Ges., **31**, 1010.
[2] *Ibid.*, **40**, 3020, 3358.
[3] THIS JOURNAL, **39**, 721.

I consider, however, that there is no *fundamental difference* between the action of alcohols and of water in all such chemical changes. Moreover, if such an unsaturated compound were really intermediate in these reactions, then formimidoester salts, $HC(=\overset{+}{N}H_2)OR$, could not be expected to yield ortho esters, because the formation of such an intermediate olefine derivative is here clearly impossible. But formimidoester salts are just exactly the ones found by Pinner to react so beautifully. Of course, we might make the assumption, using Nef's hypothesis, that a bivalent carbon derivative, $(C_2H_5O)_2C=$, is an intermediate compound in the formimidoester reactions; but I see no justification for either of these assumptions. The formation of these ortho esters, from imidoesters, is analogous to the formation of acetals from aldehydes, acids and alcohols,[1] in which reactions the formation of such an olefine derivative is impossible:

$$C_6H_5CHO + \overset{+}{H} + \overset{-}{Cl} + 2ROH \rightleftharpoons C_6H_5CHO.\overset{+}{H} + \overset{-}{Cl} + 2ROH \rightleftharpoons C_6H_5CH(OR)_2 + H_2O + HCl.$$

We find that benzamide, benzanilide, benzphenylhydrazide, which cannot form any of Diel's[2] or Staudinger's[3] corresponding intermediate ketenes, $R_2C=C=O$, discussed by Stieglitz[4] in connection with saponification, give practically quantitative yields of esters.

In view of the readiness with which such ortho esters having a group $—C(OR)_2—CH_2—$ lose a molecule of alcohol, the compound $C_2H_5OOCCH=C(OC_2H_5)_2$, obtained in the case of cyanacetic ester, most probably results, as Reiter and Hess assumed, from the loss of a molecule of alcohol from the half ortho ester of malonic acid first formed,

$$C_2H_5OCOCH_2—C(OC_2H_5)_3 \longrightarrow C_2H_5OCOCH=C(OC_2H_5)_2.$$

[1] Fischer and Giebe: Ber. d. chem. Ges., **30**, 3053; **31**, 545. Lapworth: Chem. News, **97**, 310.

[2] Ber. d. chem. Ges., **39**, 689; **40**, 355.

[3] *Ibid.*, **38**, 1735; **39**, 968, 3062; **40**, 1145, 1149; Ann. Chem. (Liebig), **356**, 51.

[4] This Journal, **39**, 613.

If the olefine derivative were the intermediate product, we should expect to obtain some ortho ester, but as a matter of fact, Reiter and Weindel were never able to isolate any. This work of Pinner, then, on the reactions of imidoester salts with alcohol, gives further evidence that our point of view is worthy of further study.

Another phase of this work is of very great importance. It is clearly very desirable to determine the dissociation constants of the alcohols corresponding to those of water measured by Kohlrausch,[1] Nernst,[2] Lewis,[3] Brönsted,[4] etc.

$$H \times OH = K_w. \quad H \times O \times H = K'_w. \quad H \times OR = K_{alc.}$$
$$H \times O \times R = K'_{alc.} \quad HO \times R = K''_{alc.}$$

The facts that glass does not dissolve readily in alcohols, and that carbonic acid does not form appreciable amounts of the conducting acid esters, $HOCOOC_2H_5$, are a great help in this work,[5] while the fact that alcohol decomposes into hydrogen and aldehyde is a great disadvantage. The aldehyde is a weak acid,

$$CH_3CHO \rightleftharpoons CH_2 = CHOH,$$

and not only would tend to act on the glass, but also tends to condense into aldol, another aldehyde which is perhaps even a stronger acid. Furthermore, both of these aldehydes may be oxidized readily into acids by the oxygen of the air. These constants for alcohol may be of very great importance, not only in a large number of oxidation and reduction reactions of the alcohols, but also in all chemical changes in alcoholic solutions in which reacting salts of weak bases or weak acids are alcoholyzed. For instance, it is obviously very important for us to know what fraction of our urazole salts is alcoholyzed when the reactions with alkyl halides are studied in alcoholic or aqueous alcoholic solutions:

[1] Z. physik. Chem., **14,** 317.
[2] *Ibid.*, **56,** 545; Z. Elek. Chem., **11,** 835.
[3] Z. physik. Chem., **55,** 449.
[4] *Ibid.*, **55,** 84.
[5] B. B. Turner: THIS JOURNAL, **40,** 558.

$$\overset{+}{Na} + \overset{-}{Ur} + HOC_2H_5 \rightleftarrows HUr + \overset{+}{Na} + \overset{-}{OR}$$
$$\overset{+}{Na} + \overset{-}{OR} + IC_2H_5 \rightleftarrows C_2H_5OC_2H_5 + \overset{+}{Na} + \overset{-}{I}$$
$$\overset{+}{Na} + \overset{-}{Ur} + IC_2H_5 \rightleftarrows C_2H_5Ur + \overset{+}{Na} + \overset{-}{I}.$$

Obviously, the relationship between the alcoholysis of the sodium urazole and the velocities of the reactions of the sodium urazole and the sodium ethylate with the alkyl halide could change so much with the different urazoles and alkyl halides that greatly varying ratios of urazole ester and ether could be obtained, and this we find to be the case. In the same way an amide salt put into alcohol may be more or less alcoholyzed and hence this alcoholysis will cause a decrease in the concentration of the reacting salt:

$$CH_3CO\overset{+}{N}H_3\overset{-}{Cl} + \overset{+}{H}\overset{-}{O}C_2H_5 \longrightarrow CH_3CONH_3OR + \overset{+}{H}\overset{-}{Cl} \longrightarrow$$
$$CH_3CONH_2 + ROH + \overset{+}{H}\overset{-}{Cl}.$$

But a knowledge of the dissociation constants of the alcohols and water is of great importance in another way which I have discussed to some extent in another paper.

SALT CATALYSIS.

When the water adds to the amide salt to form the complex cation,

$$CH_3CO\overset{+}{N}H_3 + H_2O \longrightarrow CH_3C(OH)_2\overset{+}{N}H_3 \longrightarrow$$
$$CH_3COOH + \overset{+}{N}H_4,$$

it could do so through its molecular form or the ionized portion, and the reaction velocity could be expressed approximately by the equation:

$$\frac{dx}{dt} = KC_{amide} \times C_H \times C_{H_2O} = K'C_{amide} \times C_H \times C_H \times C_{OH}.$$

Euler[1] advanced the hypothesis in 1900 that the water reacts through its ions and that salts cause the well-known salt catalysis in such reactions because they effect a corre-

[1] Z. physik. Chem., **32**, 348.

sponding change in the dissociation constant of the water. This is one of the most important questions in catalysis and work on this problem has been recorded by Arrhenius,[1] Euler,[2] Koelichen,[3] Senter,[4] Acree and his coworkers,[5] Stieglitz,[6] Reid,[7] Spohr,[8] etc. Acree and Johnson[9] considered this question and decided that the evidence was not in favor of Euler's view. Stieglitz has also taken up this question in his very important work on imidoesters and has adopted Euler's point of view, believing, with Arrhenius, that the salt cation is responsible for the salt effect. I wish to discuss this question of salt catalysis here again somewhat more fully than I did in the previous paper, especially since Lapworth,[10] one of the chief workers in catalysis, also shares in my point of view. *I believe that catalysis by salts or other neutral substances is due not so much to a change in the dissociation constant of the water as to a number of other factors of still more importance.* I consider this one of the most important phases of the mechanism of reactions, because it comes up in a large number of organic reactions, probably in most of them.

(1) I shall first discuss the evidence which leads me to believe that the views of Euler and Stieglitz are not in harmony with the facts.

(*a*) The physical chemical evidence obtained by Kohlrausch, Nernst, Lewis, Brönsted, and others is clearly against such a view. Stieglitz states that potassium chloride increases the velocity of hydrolysis of imidoester salts about 110 per cent per gram ion of potassium. Then the dissociation constant of water would have to increase from 1 to $\sqrt{2.10}$ or 1.45, an increase of 45 per cent in the dissociation of the water per gram ion of potassium.

Both Lewis and Brönsted have, by the use of the hydrogen-

[1] Z. physik. Chem., **1**, 110; **4**, 226; **31**, 197.
[2] *Ibid.*, **32**, 348; Ber. d. chem. Ges., **39**, 2726.
[3] Z. physik. Chem., **33**, 129.
[4] J. Chem. Soc., **91**, 460.
[5] This Journal, **38**, 259, 489; **39**, 226; Ber. d. chem. Ges., **41**, 3208.
[6] This Journal, **39**, 177, 467, 596, 720.
[7] *Ibid.*, **21**, 281; **24**, 397.
[8] J. prakt. Chem., **33**, 265.
[9] This Journal, **38**, 342–4.
[10] *Loc. cit.*; Chem. News, **97**, 310.

oxygen electrode in the concentration cells $H/NaOH/Ag_2O/Ag$ and $H/NaOH/HgO/Hg$, respectively, found the values for the electromotive force to be 1.224 and 1.238 volts, which agree not only with each other, but also very closely with the value 1.232 calculated by Nernst from his direct measurements of the dissociation of water. The mean of the values of Lewis and Brönsted is 1.231, which agrees very closely with that of Nernst, the maximum error being ±0.007 volt. Now Lewis and Brönsted calculated these values on the assumption that the dissociation constant of water,

$$H \times OH = H \times O \times H \times K,$$

does not change in the presence *of even* 10/*N sodium hydroxide.*

Arrhenius found that sodium chloride and potassium chloride have practically the same effect on the inversion of cane sugar. If Euler's explanation is correct, we should be able to calculate the effect of the sodium hydroxide on the dissociation of the water in Brönsted's experiment by the use of the data of Stieglitz and Arrhenius; we find that in the 4.8 N and 10.0 N solutions of sodium hydroxide *the hydrogen ion concentration should be increased nearly 300 per cent, which certainly hardly seems possible.* This would cause a change of nearly 0.02 volt in the electromotive force observed by Brönsted, whereas both his results and those of Lewis and Nernst agree to within 0.01 volt. We must remember, however, that the electromotive force varies as the logarithm of the concentration and that this method is therefore a poor one for measuring concentrations.

(*b*) If the dissociation constant of water really changes, the hydrolysis constant of the salts formed by the ester, amide, or cane sugar, and the acid, or by the ester, diacetone alcohol, etc., and alkali, would have to change correspondingly. When we consider the salt formed by the sugar and acid, we get[1]

$$C_{12}H_{22}O_{11} + \overset{+}{H} + \overline{Cl} + H_2O \rightleftharpoons C_{12}H_{22}O_{11}.\overset{+}{H} + H_2O + \overline{Cl} \longrightarrow 2C_6H_{12}O_6 + \overset{+}{H} + \overline{Cl},$$

$$\frac{dx}{dt} = K_{trans}\frac{K_b}{K_w} C_{sug} \times C_H \times C_{H_2O} = K_{trans} C_{salt\,dis.},$$

[1] Acree and Johnson: THIS JOURNAL, **38**, 306, etc.

for the velocity of transformation of the cane sugar. In this expression the factor K_w is really involved in the numerator in the C_{H_2O} and also in the denominator. These would just cancel each other and we should expect no change in the velocity constant except the *decrease* produced by the suppression of the value of C_H by the salt. But this work of Arrhenius, Spohr, Euler, Stieglitz, etc., shows that a number of salts *increase* the velocity of this hydrolysis, and others *decrease* the velocity in analogous reactions.

Koelichen found that 0.94 normal sodium thiosulphate produces a *decrease* of 4.7 per cent in the velocity of the change of the diacetone,

$$\overset{+}{K} + \overset{-}{OH} + (CH_3)_2C(OH)CH_2COCH_3 \rightleftarrows$$

$$(CH_3)_2C(\overset{-}{O})CH_2COCH_3 + \overset{+}{K} + H_2O \rightleftarrows$$

$$CH_3CO\overset{-}{C}H_2 + CH_3COCH_3 + \overset{+}{K} + \overset{+}{H} + \overset{-}{OH} \rightleftarrows$$

$$CH_3COCH_3 + CH_3COCH_3 + \overset{+}{K} + \overset{-}{OH}$$

whereas Arrhenius found an *increase* of 1.8 per cent in the velocity of saponification of esters by the same concentration of this salt:

$$CH_3COOR + \overset{+}{K} + \overset{-}{OH} \rightleftarrows$$

$$CH_3C(\overset{-}{O})(OH)(OR) + \overset{+}{K} \longrightarrow CH_3C\overset{-}{O}O + \overset{+}{K} + ROH.$$

Sodium chloride, 0.94 N, *decreases* the reaction velocity of diacetone alcohol and 0.0942 N potassium hydroxide 22.4 per cent but causes only 11.8 per cent *decrease* in the velocity of saponification of ethyl acetate with 0.025 N sodium hydroxide, and an *increase* of about 65 per cent in the inversion constant for cane sugar and 0.05 N hydrochloric acid. If we assume that the catalytic influence of the salt is due to a change in the value of K_w in such equations as the above, we are led to the contradictory conclusion that the

same salt in the same concentration can both *decrease* and *increase* this value of K_w.

(*c*) If the salt effect is due to a change in the value of K_w by the cations of the salt we should expect all sodium salts in the same ionic concentration to change the velocity of a given reaction by the same amount. But Koelichen found that in 0.94 N concentrations sodium chloride, sodium nitrate, sodium thiosulphate, and sodium sulphate produce a change of —22.4, —28.5, —4.7, and +4.9 per cent. respectively, a variation that permits of no doubt as to the above conclusion.

(*d*) One of the chief reasons for doubting the validity of Euler's and Stieglitz's belief that water necessarily enters into these reactions through its ions and that salts change greatly the dissociation constants of water and alcohols was furnished by an entirely analogous reaction in which we carefully studied just this point. When alkyl halides react with urazole salts and form esters they might be considered as reacting through the dissociated portions,

$$C_2H_5I \rightleftarrows C_2H_5^{+} + \bar{I} \rightleftarrows C_2H_4 + \overset{+}{H} + \bar{I}.$$

But we tested this question quantitatively,[1] experimentally and mathematically, and came to the conclusion that the alkyl halide most probably reacts as a molecule. Of course, the reactions are not identical, but they are analogous and both must be considered side by side.

2. I believe that salt catalysis is a very complex phenomenon caused by a combination of effects, a minor one of which may be the changes assumed by Euler.

(*a*) I believe that the catalyzing salts may combine with the reacting salts or substances and form still more (or less) reactive double salts or double compounds. Even if its concentration were small, this new double salt could account very readily for the *increase* in the reaction velocity if it had itself a large reaction velocity. But a *decrease* in the reaction velocity can be accounted for on this basis only by assuming a pro-

[1] Acree and Shadinger: THIS JOURNAL, **39**, 244; also Acree and Johnson: *Ibid.*, **38**, 262.

portionate removal of the reacting salt or compound by the catalyzing salt in the formation of the less reactive double salts or compounds, or a change in the concentrations of the reacting substances due to a change in some equilibrium point by the added substance, or by a general change in the properties of the solutions.

An enormous amount of experimental material justifies such ideas. Jones[1] and his coworkers have shown that many double salts are present in fairly large quantities in concentrated solutions. The entire change in properties of solutions of silver nitrate, cadmium and copper salts, etc., when aqueous solutions of potassium cyanide or ammonia are added, illustrate the point beautifully; and just here it has been shown quantitatively by Noyes,[2] Whitney,[3] Goodwin,[4] Bodländer,[5] Euler,[6] Küster and Thiel,[7] etc., that these changes are brought about because of the formation of such double salts as $Ag(NH_3)_2Cl$, $K_2Cu(CN)_4$, etc.

I recall here the fact that Goldschmidt[8] has shown that hydrochloric acid, sodium chloride, barium chloride, etc., or hydrobromic acid, accelerate the reduction of nitrobenzene derivatives by stannous chloride or stannous bromide because of the formation of the more reactive double salts or complex acids, $HSnCl_3$, $NaSnCl_3$, $KSnBr_3$, $HSnBr_3$, etc. Bredig[9] has shown that in the catalysis of benzoin formation by potassium cyanide, or cyanide ions, silver cyanide, barium cyanide, etc., act as negative catalyzers because they form the double salts $KAg(CN)_2$, etc., which yield fewer cyanide ions. Slator[10] has shown that silver nitrate acts as a negative catalyzer in the reaction of thiosulphate ions with alkyl halides because it forms the less reactive or less ionized double

[1] THIS JOURNAL, **19,** 83; **22,** 5, 110; **25,** 349.
[2] Z. physik. Chem., **6,** 241; **42,** 336.
[3] J. Am. Chem. Soc., **25,** 69.
[4] Z. physik. Chem., **13,** 641.
[5] *Ibid.*, **39,** 597; Z. anorg. Chem., **31,** 474; **39,** 197; **41,** 193; Ber. d. chem. Ges., **36,** 3933.
[6] Ber. d. chem. Ges., **36,** 3404.
[7] Z. anorg. chem., **24,** 57; **33,** 129.
[8] Z. physik. Chem., **48,** 435; **56,** 1.
[9] Z. Elek. Chem., **10,** 582.
[10] J. Chem. Soc., **85,** 1286; **87,** 481.

salt, $Na_2S_2O_3.Ag_2S_2O_3$. These samples serve to make clear some of the ways in which I think that positive or negative catalysis by salts or other substances may be the result, directly or indirectly, of double salt or double compound formation.

(*b*) We organic chemists have, as a rule, tried to work with dilute solutions in which *changes* in solvation, viscosity, heat of dilution, vapor tension, or osmotic pressure play a small rôle. But in a large number of the newer problems we must consider all these disturbing factors and measure their influence on the reaction velocities or reaction mechanisms. I believe that all of these factors must be considered, perhaps along with Euler's point of view, in salt catalysis.

In the last few years our physical chemists have been securing a large amount of experimental material on the influence of these various factors on the properties of solutions. Jones[1] and his coworkers have added largely to our knowledge of the relation of hydration and viscosity to conductivity. Euler[2] has shown the relation $(K—0.68)l = \text{const.}$ to hold fairly well for the relationship between the conductivity and viscosity of a solution in which K is the viscosity constant and l the equivalent conductance of the ion. Green,[3] Bingham,[4] Getman,[5] and others have recently studied the influence of fluidity on conductivity, and Washburn has brought together a very full discussion of the entire subject.[6] Now in our problems in organic chemistry we must measure both the conductivities of solutions and the reaction velocities in order to study the mechanism of the reaction and *both* of these factors are influenced by the viscosity and hydration, which are commonly ignored. Dr. Reid has found that the influence of the change in viscosity on the velocities of reactions in these aqueous alcoholic solutions is very much more marked than would ordi-

[1] For references and general literature see Carnegie Institution's Publication No. 80.

[2] Z. physik. Chem., **35**, 536.

[3] J. Chem. Soc., **93**, 2049.

[4] This Journal, **34**, 481; **35**, 195; **40**, 277; Z. physik. Chem., **57**, 193; Carnegie Institution Publication No. 80.

[5] J. Chim. Phys., **4**, 386.

[6] Technology Quarterly, **21**, No. 4, 360.

narily be supected, and in this respect he has made a very important contribution to the theory of this reaction. This change in viscosity will probably explain to a large extent all of Goldschmidt's results. Caldwell[1] has also found that both glycerine and ethyl alcohol lower the reaction velocity of sugar inversion by nitric acid very greatly. Both of these substances decrease the fluidity of water very considerably, as Prof. Jones has found in this laboratory. Lapworth[2] has found that the addition of from 4 to 30 per cent of water to a solution of hydrochloric acid and ethyl formate or methyl acetate in acetone hardly changes the reaction velocity, the tendency to increase being nearly offset by the increased viscosity of the solution of water in acetone, as found by Jones. Kistiakowsky[3] found a similar retardent effect of alcohol in esterification.

Now the reaction velocity of the salts with other substances in solution depends upon the number of *favorable opportunities* for the union of the salt with the other substance leading to the formation of the Kekulé double salt or double molecule which yields the end products of the reaction. The velocity of the reaction will therefore vary with the number of particles and their velocity, just as does the conductivity of these salts; both the reaction velocity and the conductivity must therefore vary inversely as the viscosity. Fortunately, therefore, the relation between the reaction velocity and the concentration of the salts as determined by conductivity methods is practically independent of the viscosity in most cases studied. But each should be measured in all cases and the reaction velocity and conductivity referred to the unit of viscosity.

This salt effect will therefore be dependent on the influence of the salt on the viscosity of the solution and the change this makes in the reaction velocity. The viscosity of solutions of salts in water does not vary more than a few per cent as a rule, sometimes being positive and sometimes negative, but the salt effect is sometimes very large. Potassium chloride in gram ionic concentrations decreases the viscosity of

[1] P. Roy. Soc., **78**, A. 272.
[2] Chem. News, **97**, 248, 309.
[3] Z. physik. Chem., **27**, 250.

water only about 2 per cent[1] at 25° and yet increases the velocity of hydrolysis of cane sugar by acid over 100 per cent. It is evident then that this viscosity effect found by Dr. Reid can have only a minor influence in some cases, but should be studied in all reactions.

(*c*) But Armstrong[2] has in recent years put great stress on another very important phase of salt catalysis, namely, the concentrating effect of salts due to the union of the solute with the solvent. I believe that in the inversion of cane sugar in the presence of inorganic salts contact between the reacting solute, such as the cane sugar cation, $C_{12}H_{22}O_4.\overset{+}{H}$, and the large particle of hydrated salt, such as $CaCl_2.10H_2O$, cannot be to the same extent productive of favorable opportunities for inversion as a similar collision of the sugar cation with water molecules or complexes. We can readily understand that some hydrated salts might be very active in this respect and others very inactive.

The question of solvation is of very great importance in certain other phases of the work. It is becoming realized, especially from this work of Jones, Noyes and Washburn, Buchböck, Lapworth, and Goldschmidt, that the hydrogen ions are hydrated (alcoholated) to a greater or lesser extent. Now in the hydrolysis of weak bases, like amides or esters in the presence of acids, the hydrogen ions are competed for by the ester (amide), alcohol, and water. The equilibrium conditions are therefore very complex and it would be practically impossible to know the concentration of the free hydrogen ions at any moment. We have thought of using the hydrogen electrode in connection with conductivity methods, on the supposition that only the free hydrogen ions are in equilibrium with the electrode. This would enable us to get some measure of the actual amount of amide or ester salt, hydrated or alcoholated hydrogen ions, and free hydrogen ions. Denham's[3] work on aniline hydrochloride has suggested the applicability of such methods and Mr. Desha is

[1] Bousfield: Z. physik. Chem., **53**, 309.
[2] P. Roy. Soc., **78**, A, 272; **79**, 564; **81**, 80.
[3] J. Chem. Soc., **93**, 41, 424; Z. anorg. Chem., **57**, 361.

now engaged on this problem. The method, however, is complicated by many difficulties which Prof. Denham has kindly privately informed us that he, too, experienced.

(*d*) Finally, one other salt effect must be considered. The thermodynamic potential, or "activity," or driving force behind each reaction depends not only upon the substances themselves but upon the surrounding *field*. When this is changed by the addition of electrolytes or nonelectrolytes there will be a change in the corresponding thermodynamic potential and therefore in the reaction velocity, although this will in many cases be negligible. Our physical chemist colleagues must give us the aid needed here. Perhaps we shall secure aid from electromotive force measurements in reversible and irreversible reactions, such as those studied by Schoch,[1] Lewis, and many others, from heats of reaction, and other necessary data.

These and many other things influence the velocities of reactions, and much work will be necessary to clear up the many perplexing uncertainties of chemical changes.

JOHNS HOPKINS UNIVERSITY,
BALTIMORE,
May 8, 1909.

THE ALCOHOLYSIS OR ESTERIFICATION OF ACID AMIDES.

BY E. EMMET REID.

(I have been aided by a grant to Prof. S. F. Acree from the Carnegie Institution in carrying on this work.)

Two of the best known reactions in organic chemistry are the esterification of acids and the hydrolysis of amides:

I. $C_6H_5CO - OH + HOC_2H_5 = C_6H_5COOC_2H_5 + H_2O$,

and

II. $C_6H_5CO - NH_2 + HOH = C_6H_5COOH + NH_3$.

If, now, as appears from the formulae above, benzoic acid and benzamide are analogously constituted derivatives of

[1] THIS JOURNAL, **41**, 208, 232. J. Chem. Soc., **29**, 314. Trans. Am. Elec. Chem. Soc., **11**, 135.

water and ammonia, H—OH and H—NH_2, which are undoubtedly analogous in many of their reactions, and if water and alcohol are analogous, then alcohol should act on benzamide to give the ester:

III. $C_6H_5CO — NH_2 + HOC_2H_5 = C_6H_5COOC_2H_5 + NH_3$.

When I mentioned to Professor Acree my intention of trying this reaction, he at once said that he had predicted it from his point of view of catalysis, particularly with reference to amide salts, and that it would be found to go in a manner similar to the reactions of hydroxylamines, hydrazines, and amines on amides and analogous substances, and to Pinner's formation of ortho esters from imidoester salts. My experiments have shown results in harmony with his views.

Reaction (1) is commonly accelerated by a catalytic agent such as hydrochloric acid. Accordingly some *p*-nitrobenzamide was dissolved in absolute alcohol and dry hydrochloric acid passed in. After a few minutes' warming, on pouring the mixture into water, a precipitate was obtained which, on being freed from unchanged amide by washing with hot water, showed the melting point, 57°, and other properties of ethyl *p*-nitrobenzoate. Hence the above reaction does take place and an amide may be esterified under the same conditions, and with the same facility, as the corresponding acid. This appears as the reversal of the well-known reaction by which an amide is made from the ester and ammonia.

Quantitative experiments showed that at 50° the reaction proceeded at a rate convenient for measurement. Accordingly measurements of the reaction velocity were undertaken, using benzamide and the three nitrobenzamides in absolute alcohol, with hydrochloric acid as a catalytic agent. Some little work has been done also in alkaline solution, but so far without definite results. Since beginning this work I have come across that of Guareschi,[1] who heated benzamide and phenol to the boiling point of the mixture and got phenyl benzoate among other things. His point of view and method of work were entirely different from mine.

[1] Ann. Chem. (Liebig), **171**, 141.

A considerable amount of work has been done, but before the subject can be cleared up it must be taken up in a more comprehensive way and the work extended in a number of directions. In order to reserve the field for myself until some, at least, of this work can be done, I have thought best to publish some of the results so far obtained.

Method of Work.

The required amount of the amide was weighed into a flask holding about 12 cc. These flasks were specially blown with long narrow necks. Beginning with Series VI., test tubes were used. These test tubes were heated with dilute hydrochloric acid for two days before use. They serve well for this purpose for, on account of the thinness of the glass, they may be put into the flame directly and can then be cooled quickly. After the solid was weighed in, the test tube was drawn down to a narrow neck through which the pipette passed. The alcoholic hydrochloric acid was kept for at least three minutes in a pipette jacketed with water at 50° C. After running in this solution the flask was corked up, or the test tube sealed off, and plunged, with vigorous shaking, into the water bath at 50°. These operations, altogether, usually required less than one minute. The amide dissolved quickly. The tube was drawn off at such a point as to leave little air space over the solution. To stop the reaction the contents of the flask, or test tube, were poured into cold water containing nearly enough caustic soda to neutralize the acid present.

The ammonia from each sample was distilled with magnesium hydroxide into N/10 hydrochloric acid. The excess of acid was titrated back with N/10 alkali, with cochineal as indicator. When the neutral point was reached the burette containing the acid was also read and an unknown amount of the acid run into the flask containing the distillate. This was again neutralized with the alkali and both burettes again read. This process was repeated. Thus the estimation of the ammonia in the distillate was made to depend on three

independent titrations. These usually agreed quite closely. The mean of the three was always taken.

The magnesium hydroxide was made each time by adding 5 cc. of 5 N magnesium chloride and 5 cc. 2.5 N caustic soda to the nearly neutralized sample in the distillation flask. Experiment showed that when weighed samples were distilled the usual time, 70 minutes, under the usual conditions, with magnesium hydroxide, 0.25, 0.5, and 0.6 per cent of benzamide, meta-, and paranitrobenzamides, respectively, were decomposed. Accordingly, x, the percentage of decomposition found, was diminished by 0.25, 0.5, or 0.6 per cent of 100—x, according to the amide used.

The amides used were carefully purified by repeated crystallization, the last time from conductivity water. The alcohol used in Series I. to III. was commercial absolute alcohol of about 99.5 per cent. The other series were made with 99.78 per cent alcohol, prepared by double distillation from lime. The strength of the alcohol was determined by the kerosene test.[1] The dilute alcohols were made by adding weighed amounts of water to weighed amounts of the 99.78 per cent alcohol into which dry hydrochloric acid had been passed. A common stock solution was made up for each series. A portion of this was measured at 50° from the pipette in the usual way, weighed, and titrated to obtain the value of A for that series.

The great influence of water on the speed of the reactions was not considered in the earlier work, and sufficient care was not taken to prevent its absorption. This may account for some of the erratic results. The temperature was 50°.05 C. with a variation of one or two hundredths either way, except in Series XII. and XIII., in which it was 50°.19 C. The volume of the sample was 10.34 cc. except in Series XII. and XIII., in which it was increased to 20.67 cc. on account of the smaller solubility of the benzamide in water.

The analytical data have been substituted in the usual formula for a bimolecular reaction,

$$K = \frac{2.3025}{(A-B)t} \log. \frac{(A-x)B}{(B-x)A}.$$

[1] Andrews: J. Am. Chem. Soc., **30**, 353.

A is the concentration of the hydrochloric acid, B that of the amide used, both in terms of volume molecular normal, while t is the time in minutes, and x the corrected percentage of the amide decomposed. Since A and B appear in like powers in both the numerator and denominator of the fraction in the last portion of this expression, for convenience of calculation B was taken as 100 per cent and A as the proper multiple of this.

The closeness with which the reaction obeys the bimolecular formula may be seen from the values of K taken from Series VI. and VII.:

Series VI.	1084	1079	1084	1074
Series VII.	1046	1043	1044	1036

The agreement in Series XI. and XII. for benzamide is equally good. These are the only series made under the best conditions. The amounts of ammonia found in some of the shorter period samples, particularly for benzamide, are too small for good analytical work. One per cent decomposition gives only 0.5 mg. ammonia or 0.3 cc. N/10 acid. In some of the analyses given the amount of N/10 acid neutralized was only about 0.60 cc. The errors of titration, etc., may be a considerable per cent of this small amount. In all of the tables the real value of K is multiplied by 1,000,000 to avoid decimals.

The formation of ethyl chloride diminishes the strength of the acid somewhat, but this effect is considerable only in long time periods, and even in these periods, with amides which decompose rapidly, the most of the amide has already reacted before the acid loses much of its strength. Samples of the acid used in Series VI. and VII. were heated for 12 and 36 hours in sealed tubes at 50° and were found to lose strength at the rates of 0.27 and 0.26 per cent, respectively, per hour. In the present work it has not been thought worth while to introduce corrections for this into the calculations, though nearly all the values of K for long time periods show a falling off which may be accounted for in this way. Cain's[1]

[1] Z. physik. Chem., **12**, 751.

work indicates a more rapid formation of ethyl chloride at 50° though none of his work was done at this temperature. The conditions of his experiments were, however, quite different.

The first thing to be found out in the experiments was whether the reaction was really of the second order. Determinations running all the way from 2 to 75 per cent decomposition show that the equation holds over at least this range. The next matter was to contrast the different amides with each other with the same and with different concentrations of acid. Series were run with concentrations of acid from 0.4 to 3.7 N, in order to determine the influence of this factor on the velocity.

Series I.—*A* 3.640 N, *B* 0.1934 N, Alcohol 99.5 per cent.

m-Nitrobenzamide.

t	30	60	90	120	240	480	Average.
x	7.32	13.07	19.50	26.04	44.72	68.77	
K	697	643	665	699	686	702	682

p-Nitrobenzamide.

x	8.58	15.79	23.06	29.14	48.26	73.54	...
K	832	790	805	792	774	787	797

Series II.—*A* 2.870, *B* 0.1934, Alcohol 99.5.

m-Nitrobenzamide.

t	90	120	150	240	420	450	480	510	Av.
x	...	...	...	43.76	60.51	64.66	...	...	
K	...	...	...	849	800	827	...	...	824

p-Nitrobenzamide.

x	21.76	27.76	33.39	45.07	...	69.82	71.28	73.83	
K	958	950	956	942	...	955	932	944	950

Series III.—*A* 0.3967, *B* 0.2903, Alcohol 99.5.

Benzamide.

t	90	120	240	480	16h	24h	48h	Average.
x	1.42	2.12	3.61	6.41	10.04	10.55	36.16	
K	404	(454)	391	(356)	407	398	404	400

For brevity we will designate the constants (K) for meta- and paranitrobenzamides as K_m and K_p, and that for benzamide as K_b. From Series I., $K_p/K_m = 1.17$ and from Series II., 1.15. These values are very near to the ratio

of the hydrolysis constants for the same amides, namely, 1.20.[1] Goldschmidt[2] finds for the esterification of meta- and paranitrobenzoic acids the ratio $K_p/K_m = 1.20$.

For further discussion the average values of the various constants are brought together in the following table, several being taken from the series given below. The first column gives the number of the series from which the results are taken. Under N is the strength of the acid in such series and under V the reciprocal of N. The series are so arranged that V, the volume of solution containing a gram molecule of hydrochloric acid, increases from top to bottom. In the next column is found the molecular conductivity, and in the last three columns are given the quotients obtained by dividing the several values of K by the molecular conductivity.

It appears that K_m/K_b is 4.5 with 1.5 N acid, but only 3.7 with 1 N acid and even lower with weaker acid. One determination, not included in the series given, indicates that this ratio is much higher with the 3.6 N acid. K_m/K_b for the hydrolysis of these two amides in water solution is 0.94, the benzamide being hydrolyzed even faster than the *m*-nitrobenzamide.

Table I.

Series.	K_m.	K_p.	K_b.	N.	V.	$m.c.K$	$m/m.c.$	$K_p/m.c.$	$K_b/m.c.$
I.	682	797	...	3.64	0.275	6.2	110	129	..
II.	825	950	...	2.87	0.348	7.0	118	136	..
IV.	987	...	220	1.52	0.658	8.6	115	...	25
VI.	1080	...	288	1.09	0.911	9.5	114	...	30
III.	....	...	400	0.397	2.52	12.3	...	...	33

That benzamide, a derivative of ammonia, is a real base is shown by the existence of many of its salts. It forms well-defined salts even with weak acids. Its oxalate, tartrate, and succinate have recently been prepared by Henle.[3] It will exist then in hydrochloric acid solution in four forms, the amide, its hydroxide, its hydrochloride, and the cation, $C_6H_5CONH_3^+$, derived either by the dissociation of the salt

[1] Reinsen and Reid: THIS JOURNAL, **21**, 281.
[2] Z. Elek. Chem., **15**, 9.
[3] Ber. d. chem. Ges., **38**, 1373.

or by the direct combination of the hydrogen ions with the free base. The case of acetamide has been thoroughly worked out mathematically and the conclusions verified experimentally by Acree and Nirdlinger.[1] They conclude that the rate of decomposition would be infinitesimal if the amide itself were the reacting substance. The same reasoning applies to the hydroxide of the amide as it is also present in pure water solution in somewhat the same proportion to the amide as it is in acid solution. They show that if the undissociated salt were the reacting substance the reaction velocity, K, should be inversely proportional to the concentration of the acid, while if the complex cation is the chief, or sole, reacting substance the velocity of the reaction must conform to the well known bimolecular reaction formula.

That the bimolecular formula is applicable may be shown in the following somewhat different manner. Assume that the complex cation is the reactive substance. Then the reaction will be a monomolecular one with regard to this cation and hence will obey the monomolecular law, $\frac{dx}{dt} = yk$, in which y is the amount of this ion at the time, t. We do not know anything about the magnitude of y, but we do know that it is a certain fraction of the amount of amide present at that time. If B is the original concentration of the amide, the amount of it present at the time, t, will be $B - x$, so we may put $y = (B - x)s$ in which s is this fraction. Now s in this expression involves two things, namely, the affinity constant, or salt-forming power, of the amide and the concentration of the hydrogen ions at that time. The affinity constant being constant for a given amide, we may replace s by $[\overset{+}{H}]b$, in which b is a constant for the amide. This assumes that the equilibria between the amide, its salt, and the ions of the salt are instantly adjusted, as is usually the case with that class of equilibria. But $[\overset{+}{H}]$, the concentration of the hydrogen ions, equals $a(A - x)$ in which $(A - x)$ is the concentration of acid and a is the fraction of the acid

[1] This Journal, **38**, 489.

which is dissociated at that time. If the conditions are such that the percentage of ionization of the acid does not change much during the reaction, a is sensibly constant. Then we may put $\frac{dx}{dt} = ab(A - x)(B - x)k = (A - x)(B - x)K$, as the product of three constants is a constant. Reactions of alkyl halides, acylhalogenaminobenzene derivatives, and oximes have been treated by Acree and his coworkers[1] in a precisely analogous manner.

In the above we may use the value of a as determined in pure water solutions of hydrochloric acid, provided the amide present is an extremely weak base or is present in very small quantities relative to the acid. Acree and Nirdlinger saw clearly the importance of a knowledge of the strength of the amide base so as to be able to calculate the amount of salt formed and the change in dissociation of the acid. They proposed to measure this strength so as to be able to make these calculations. They did make a few measurements as to the amount of salt formed and found it to be only a few per cent of the amount of amide present.

That the hydrolysis of amides conforms to the bimolecular reaction formula was first shown by Ostwald[2] for acetamide and ten years ago by Remsen and Reid[3] for benzamide and twenty-four substituted benzamides, and recently by Crocker[4] for seven fatty amides. None of these authors was particularly concerned with the mechanism of the reaction. Acree and Nirdlinger were the first to study it with particular reference to intermediate compounds, such as salts and their ions. By varying the concentrations of the amide and the acid they obtained considerable evidence that the complex cations are chiefly, if not solely, concerned in the reaction.

This is here accepted as the mechanism of hydrolysis. For the history and development of this theory as applied to catalysis in general, and for full references to the articles of all who have worked upon it the many papers on catalysis

[1] THIS JOURNAL, **38**, 258 and 489; **37**, 410; and **39**, 228, 237–47.
[2] J. prakt. Chem., **135**, 1.
[3] THIS JOURNAL, **21**, 281; **24**, 397.
[4] J. Chem. Soc., **91**, 952.

by Professor Acree and his students[1] must be consulted. It remains here to adapt this theory to the facts brought out in Table I., particularly as relates to the different behavior of benzamide and the nitrobenzamides.

Benzamide, being decidedly basic, will combine quite largely, relatively to the nitrobenzamides, with the hydrogen ions, even with a moderate excess of acid and a moderate concentration of hydrogen ions, and hence an increase in the concentration of the acid will not produce a proportionate increase in the concentration of the complex ion. Hence its reaction rate, which depends on the amount of the complex ion, will not increase proportionately with increased acid concentration. That it does not appears from the last column of the table. The nitrobenzamides, being far weaker bases, will, in a given concentration of acid, form far less of these complex ions, but, the amide concentration remaining the same, the amounts of these complex ions in various concentrations of acid will be closely proportional to the concentration of the hydrogen ions, even over a wide range of dilution. The ionization of the acid as found in the pure solvent may be used with little error. Thus the conductivity of hydrochloric acid in water increases only slightly when it is diluted from one volume to two but the conductivity of acetic acid nearly doubles for the same dilution. This all follows from the application of the mass law to these equilibria, as has been discussed by Acree, Bredig, Stieglitz, Lapworth, Goldschmidt, and others.

That a considerable combination of *p*-nitrobenzamide with something in the solution does take place with high concentrations of acid, and only with high concentrations, is shown by the fact that the desired amount of this amide dissolved quickly in the concentrated acid of Series I. and II., but with the same volume of the 0.4 N acid of Series III., long shaking effected solution of only a fraction of this amount. The use of this amide had to be discontinued on this account.

Data as to the ionization of hydrochloric acid in alcohol

[1] This Journal, **28**, 370; **37**, 71, 410; **38**, 258, 489, 746; **39**, 145, 226, 300; J. Am. Chem. Soc. **30**, 1755; Ber. d. chem. Ges., **41**, 3199.

are scarce, and the value of the older work has been made doubtful by the recent work of Goldschmidt[1] showing the great influence of even small amounts of water on the conductivity of such solutions. The following data as to the conductivity of hydrochloric acid in alcohol have been taken from the work of Kablukoff,[2] (1) $v = 0.55$, $\mu = 8.11$; (2) $v = 0.98$, $\mu = 9.40$; (3) $v = 1.17$; $\mu = 10.59$; (4) $v = 2.37$, $\mu = 13.24$. These are plotted on the accompanying diagram and a smooth curve drawn, extending to the origin, compromising the several determinations. From this curve the values

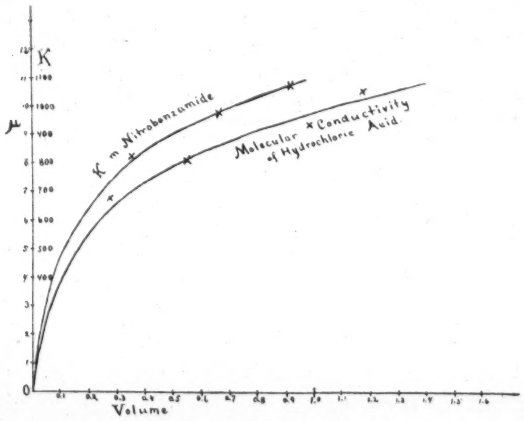


Fig. I.

for molecular conductivity for the required volumes have been taken off and inserted in the above table. The quotients in the following columns show that the rates of alcoholysis for meta- and paranitrobenzamides are very nearly proportional to the hydrogen ion concentration in the various solutions. The low values for the constants (K) of the first series may be, at least partly, explained by the fact that this

[1] Z. Elek. Chem., **15**, 6.
[2] Z. physik. Chem., **4**, 429.

solution of hydrochloric acid in alcohol was made several weeks before it was used and was not guarded from the moisture of the air. All others were used as soon as possible after making. The values of the several constants are plotted and a curve drawn for comparison. If the constants for the nitro-amides follow the curve, those for benzamide can not.

From Series IV. below it appears that the nitro group in the ortho position exercises the same remarkable retarding influence as it does in hydrolysis of amides and in esterification of acids.

After these first three series had been made the work of Goldschmidt[1] and Lapworth[2] on the influence of small quantities of water on esterification velocities of acids raised the question as to what that influence might be on the esterification velocities of amides. Series IV. and V. were run to decide this question. The group of five series following was made to carry this over a greater range.

Series IV.—*A* 1.520, *B* 0.2903, Alcohol 99.78.

Benzamide.

t	60	120	240	480	Average.
x	2.19	3.90	7.61	14.76	
K	(245)	219	219	221	220

m-Nitrobenzamide.

x	8.74	16.53	29.11	48.35	
K	1013	1008	972	955	987

o-Nitrobenzamide.

x	...	...	1.29	3.03	
K	...	...	36	42	39

Series V.—*A* 1.502, *B* 0.2903, Alcohol 97.67.

m-Nitrobenzamide.

t	60	120	240	480	Average.
x	6.67	12.81	23.33	40.87	
K	770	770	753	762	764

[1] Z. Elek. Chem., **15**, 4, and Z. physik. Chem., **60**, 749.
[2] J. Chem. Soc., **93**, 2187.

Series VI.—*A* 1.094, *B* 0.2903, Alcohol 99.78.

Benzamide.

t	60	120	240	480	Average.
x	2.13	3.58	7.17	14.07	
K	(331)	282	288	295	288

m-Nitrobenzamide.

x	6.56	12.96	24.02	41.12	
K	1084	1079	1084	1074	1080

Series VII.—*A* 1.0909, *B* 0.2903, Alcohol 99.48

Benzamide

t	60	120	240	480
x	2.09	3.61	7.06	13.85
K	324	280	282	290

m-Nitrobenzamide.

x	6.77	12.56	2 3.23	40.00
K	1046	1043	1044	1036

Series VIII.—*A* 1.085, *B* 0.2903, Alcohol 98.77

Benzamide.

t	240	480	960	1920
x	6.27	13.17	24.20	48.28
K	251	276	275	282

m-Nitrobenzamide.

x	20.81	35.43	57.25	...
K	923	946	896	...

Series IX.—*A* 1.070, *B* 0.2903, Alcohol 97.57

Benzamide.

t	120	240	480	960	1920
x	...	5.83	12.21	22.55	40.54
K	...	236	258	257	269

m-Nitrobenzamide.

x	9.28	17.79	30.81	48.50
K	768	782	756	698

Series X.—*A* 1.047, *B* 0.2903, Alcohol 93.93.

Benzamide.

t	240	480	960	1920
x	4.81	9.64	18.64	33.99
K	198	204	211	218

m-Nitrobenzamide.

x	11.46	21.18	37.02
K	492	489	456

Series XI.—*A* 1.0068, *B* 0.2903, Alcohol 88.59.

	Benzamide.	*m-Nitrobenzamide.*	
t	480	480	960
x	7.82	14.99	7.05
K	170	344	340

The values of the constants for benzamide, K_b, as found for the 8- and 16-hour periods, and those for *m*-nitrobenzamide, K_m, for the 4- and 8-hour periods, have been considered in making out the following table. From the trend of these, when plotted against the percentage of water present in the various series, 296 has been assumed as the value of K_b in perfectly anhydrous alcohol and 1120 as the value of K_m in the same. It is intended to verify these by actual experiment with perfectly anhydrous alcohol. In the first column is given the percentage of water calculated from the weights of water and alcohol present, in the next the molecular percentage of water, then the value of the constant for benzamide and the percentage of retardation, then the same for *m*-nitrobenzamide.

Table II.

Per cent water.	Mol. per cent.	K_b.	Per cent ret.	K_m.	Per cent ret.
0.00	0.00	296	0.0	1120	0.0
0.22	0.59	291	1.7	1080	3.7
0.52	1.32	286	3.4	1042	7.0
1.23	3.05	276	6.7	934	16.6
2.43	5.94	258	12.8	769	31.4
6.07	13.92	207	30.1	491	56.1
11.41	24.55	170	42.5	342	69.5

These results show the enormous influence of water on the velocity of the decomposition of the amides. They are based on the amount of ammonia found, and hence of amide decomposed, regardless of whether it went into the ester or into the acid. The effect of the water is quite different in amount for the two amides. The effect of water on the esterification of amides is quite like its effect on the esterification of acids.

In order to compare these results with the effect of water on the esterification of acids, the values of "K" given below

have been taken from Goldschmidt's work.[1] The units are different but they are comparable among themselves. They were obtained with very much weaker acid than was used with the amides, hence are comparable only in a general way. The amounts of water are those used by Goldschmidt, calculated in percentages by weight. The data for the amides are taken directly or by interpolation from Table II., above. Goldschmidt's values of K' are taken for the shortest time periods, the ones that suffer least from the accumulation of water during the reaction. R_b, R_m, and R_a are the retardations of the esterification of benzamide, *m*-nitrobenzamide, and benzoic acid, respectively, produced by the stated amounts of water. These are calculated as percentages of the maximum rates.

Table III.

Water	0.00	0.22	0.45	0.90
K_b	296	291	287	281
R_b	..	1.7	3.0	5.0
K_m	1120	1080	1051	989
R_m	..	3.7	6.2	12.1
K'	220	188	148	104
R_a	..	14.5	32.7	52.7
R_m/R_b	..	2.2	2.1	2.4
R_a/R_m	..	4.0	5.3	4.3

It appears from this comparison that the effects of like amounts of water on the rates of esterification of these three compounds are strictly comparable. It is several times greater with one than with another but the effect seems to be of the same order in all three cases and the proportionality is maintained as the amount of water increases. This accords perfectly with the theory if we assume, with Kastle, Bredig, Lapworth, Stieglitz, and Acree, that the hydrogen ion unites with the benzoic acid to form a complex cation, as it does in the case of the amides. For much evidence on this view see the article of Acree and Johnson.[2] The weaker the base of a salt, the greater the amount of its hydrolysis, or decomposition, by a given amount of water. This is well

[1] Z. physik. Chem., **60**, 749.
[2] This Journal, **38**, 258.

understood in the case of such salts as aluminum and antimony chlorides. If benzamide, *m*-nitrobenzamide, and benzoic acid all form hydrochlorides, these salts will all be more or less unstable and will be decomposed by water, the amount of the decomposition decreasing in the order given, since *m*-nitrobenzamide is a weaker base than benzamide, and benzoic acid, as a base, is far weaker still. The ions of a salt are always in equilibrium with the undissociated salt. As the velocity of the reaction depends on the concentration of the cation of this salt, it will ultimately, though not directly, depend on the amount of the salt present in the solution, undissociated as well as dissociated. That alcohol may decompose salts in an analogous way is generally assumed. From recent work of Lapworth,[1] it would appear that alcohol is far less efficient than water in this reaction.

After making these experiments, it appeared interesting to compare the effect of alcohol on the rate of hydrolysis with the influence of water on the rate of alcoholysis. Accordingly the following determinations were made with benzamide. Only half the usual concentration of the amide could be used on account of its smaller solubility in water.

Series XII.—*A* 0.9600, *B* 0.145, Water 100 per cent.

t	20 h.	36 h.	38 h.	60 h.	Average.
x	22.16	37.24	38.96	53.84	
K	(225)	232.5	233.8	235.3	234.5

Series XIII.—*A* 0.9665, *B* 0.1451, Alcohol 8.05, mol. per cent 5.67.

x	19.29	34.25	47.85	...
K	(188)	196.4	195.6	196.0

From the average of the 38- and 60-hour experiments the retardation produced by the alcohol is 16.4 per cent. The two 20-hour samples were heated at a different time and, by an accident, the temperature went too low for a part of the period. Hence they are not to be compared with the others as to the value of *K*, but when compared with each

[1] J. Chem. Soc., **93**, 2187.

other, they show a retardation of 16.2 per cent. I have since found that a like amount of alcohol retards the hydrolysis of benzamide by barium hydroxide to about the same extent. In the reaction mixture of every sample of Series XIII. ethyl benzoate was easily detected. Hence esterification, or alcoholysis, of the amide goes on in presence of a very large excess of water.

If on a diagram we plot the rate of decomposition of benzamide, whether alcoholysis or hydrolysis, with regard to the amounts of water and alcohol present, the curve is seen to sag rapidly at each end (Fig. II.) If molecular percentages

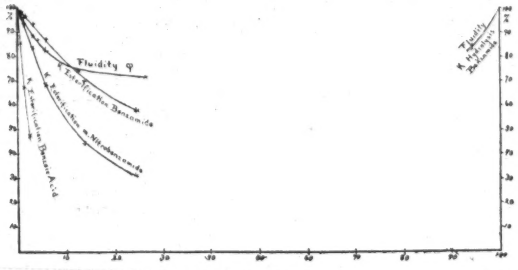


Fig. II.—Influence of water on rates of reactions.

are considered, the two ends of the curve show a marked resemblance to each other. In a conversation with Professor Jones, there was brought out the resemblance of this curve to the fluidity curve of mixtures of alcohol and water as drawn by Jones and Carroll.[1] Accordingly viscosity measurements were made on the acid solutions used in Series XII. and XIII. These did not contain the amide. Measurements were made with an Ostwald viscometer.[2] The viscosities at 50° for the two solutions were found to be 0.00590 and 0.00699. Taking the reciprocals of these as fluidities, we find that the fluidity of the water-alcohol solution is 84.4 per cent of the fluidity

[1] Carnegie Institution Publication No. 80.

[2] Ostwald and Luther: Physiko-chemische Messungen, p. 260.

of the pure water solution. Thus the presence of this quantity of alcohol reduces the fluidity 15.6 per cent and retards the reaction 16.3 per cent. The increase in viscosity apparently accounts for much of the decrease in the speed of the reaction. The close numerical agreement in this case is regarded as accidental. That there are other important factors is certain. This will be considered more fully further on.

The solutions with which Series VI. to XI. were made had been used up, but a series of others were prepared of nearly the same proportions, strength of acid, etc. A 10 cc. sample of each was taken and 363.3 mg. of benzamide, the amount used in the regular determinations, dissolved in it. The viscosities of these mixtures were measured at 50°. From these measurements the viscosity for no water was found by extrapolation. The amounts of retardation are taken from Table II. above, either directly or by interpolation. The concentration of the amide was in each case 0.295. The results are tabulated in Table IV.

Table IV.

Per cent water.	Mol. per cent.	Conc. HCl.	Viscosity.	Fluidity.	Per cent dec. of φ.	Per cent retard.
0.00	0.00	1.070	0.00957	104.5	0.0	0.0
0.22	0.59	1.072	0.00975	102.6	1.8	1.7
0.44	1.09	1.068	0.00993	100.7	3.6	3.1
1.29	3.20	1.048	0.01082	92.4	11.6	7.0
1.71	4.26	1.065	0.01100	90.0	13.0	9.9
2.42	5.94	1.028	0.01152	86.0	17.7	12.8
6.00	12.75	1.075	0.01292	77.6	26.0	29.8
12.50	27.00	1.129	0.01341	74.6	28.6	45.0

As we pass from alcoholic to water solutions, hydrolysis gradually replaces alcoholysis. When the water molecules begin to be a considerable proportion of the whole number, this partial substitution of K_h, the hydrolysis velocity, for K_a, the alcoholysis velocity, will produce a sensible lowering in the average velocity. As we pass from the one medium to the other there is a change in the degree of dissociation of the hydrochloric acid, and a general shifting of all equilibria. The concentration of the amide salt and its degree of dissocia-

tion must change. All of these changes are, doubtless, more or less gradual, depending on the gradual increase in the proportion of water molecules. In the case of the amides here worked with, for small additions of water to alcohol, or *vice versa*, the changes in viscosity seem able to account very largely for the observed changes in reaction velocities. With much larger additions, changes in viscosity continue to account for an important proportion of the observed retardations.

The extensive and important work of H. C. Jones and his coworkers[1] on viscosity in relation to conductivity of electrolytes in mixtures of solvents has shown the great influence of viscosity on conductivity. The recent work of Green,[2] in which the viscosity of conducting solutions was intentionally increased, shows the same. The above results suggest that a knowledge of the viscosity of the media in which reactions take place is fundamental to an estimate of the real value of the velocity constants. Thus at 50°, with hydrochloric acid, for benzamide, K_h for pure water is 234, while for alcoholysis in pure alcohol, K_a is 296. Plainly these constants are not directly comparable since the hydrolysis was measured in a solution whose viscosity was 0.00590, while the viscosity with which the molecules had to contend in the alcoholysis was 0.00957. From now on I intend measuring the viscosity of every solution in which I measure a reaction velocity. I hope to study the influence of viscosity on these and other reactions.

In the case of an amide in the presence of both alcohol and water, alcoholysis and hydrolysis go on parallel. Thus we have the two reactions:

$$C_6H_5CONH_2 + H_2O = C_6H_5COOH + NH_3,$$

and

$$C_6H_5CONH_2 + HOC_2H_5 = C_6H_5COOC_2H_5 + NH_3.$$

So far only a little work has been done on the comparative rates of the two reactions in mixtures of alcohol and water.

With a sample of 498.4 mg. of *m*-nitrobenzamide which

[1] "Viscosity and Conductivity," H. C. Jones and others: Carnegie Institution Publication No. 80. Also numerous journal articles.

[2] *J. Chem. Soc.*, **93**, 2049.

was heated seven days with the 93.93 per cent alcohol of Series X., the ammonia found showed 86.97 per cent decomposition of the amide. The ester and acid were extracted with ether and the acid titrated. This accounted for 4.58 per cent. The ester was heated with water and allowed to solidify in a lump. This, after drying, weighed 489 mg. Its melting point was low, and it was again heated with water. This brought its melting point up to 42°, the correct value. The water extract was distilled with strong caustic soda, and ammonia corresponding to 10 mg. of the amide was found. Subtracting 10 from 489 gave 479 as the correct weight of the ester. This corresponds to 82.97 per cent of the amide, making 86.89 per cent of the 86.97 per cent of the amide decomposed. This is of interest as showing that alcoholysis is a clean reaction and that alcoholysis and hydrolysis may be studied in the same solution and their rates compared. The ratio of ester and acid found in this experiment is not to be taken as representing the true ratio of the rates of their formation, as in the long time which this sample was heated some of the ester may have been saponified, or the reverse.

By extracting the acidified distillation residues and titrating the extracted benzoic acid, the amounts of hydrolysis in some of the samples of Series X. and XI. were determined. Allowance had to be made for the ethyl benzoate saponified during the distillation with the magnesium hydroxide. As this allowance was considerable and somewhat uncertain, the results are only approximate. The results give the hydrolysis in percentages of the total amide decomposed. For the four benzamide samples of Series X. with 13.92 molecular per cent of water, these values are 11.6, 11.5, 14.2, and 13.0, average 12.6 per cent; and for one sample of Series XI. with 24.55 molecular per cent of water present, 17.5 per cent; that is, the alcoholysis went on 7.9 times as fast as the hydrolysis in the first case, and 4.6 times as rapidly in the other.

In order to explain the enormous influence of small amounts of water on the velocity of esterification Goldschmidt[1] and Lapworth[2] have recently put forward theories which they

[1] Z. Elek. Chem., **15**, 4.
[2] J. Chem. Soc., **93**, 2187.

support with mathematics and a mass of experimental data. Goldschmidt assumes that the reactive substance in catalysis of this sort is the ion $C_2H_6\overset{+}{O}H$, formed by union of the hydrogen ion with a molecule of alcohol. According to his theory, when water is introduced, the $\overset{+}{H}$ hydrogen ion leaves the alcohol and goes to the water to form $H_2\overset{+}{O}H$ ions. Thus the amount of this change depends on the amount of water added.

Lapworth assumes that the $\overset{+}{H}$ ions are the active agents in such reactions and that as water is added these combine with water molecules to form $H_2\overset{+}{O}H$ ions which are inactive so far as esterification, etc., are concerned. He concludes that real $\overset{+}{H}$ ions are extremely scarce in water solution.

The extensive work of Jones[1] and his students on hydrates in solution all goes to show that salts are commonly hydrated in solution and that ions are probably still more hydrated. The work of Washburn[2] serves to emphasize the hydration of ions. Carrara[3] recognizes the possibility of alcoholation as well as hydration of ions. The work of Jones further shows that in alcohol the salts are *solvated* as they are in water. The reciprocal relations of water and alcohol are beautifully shown in Plate XVI. of the work of Jones and Anderson[4] on neodymium chloride in mixtures of methyl alcohol and water. In water solution certain bands exist, in alcoholic solution, certain others, distinct in character and location. They say: "In every case where the alcoholic solution has a strong band . . . we begin to see traces of this band when the proportion of alcohol in the mixture reaches 50 per cent." "The band belonging to the aqueous solution may be seen very clearly even in the strip corresponding to the 2.6 water solution. . . . " "On Plate XVI. the two sets of bands coexist, the bands due to the aqueous solution decreasing, while those belonging to the alcoholic solu-

[1] Carnegie Institution Publication, 60, also numerous journal articles.
[2] J. Am. Chem. Soc., **31**, 322.
[3] Ahrens' Sammlung, **12**, 413 (1908).
[4] THIS JOURNAL, **41**, 185, 276.

tion increase in intensity with decrease in the percentage of water; . . . the two sets of bands have about half their full intensity in a solution containing about 8 per cent. of water." Plate III. for cobalt chloride in mixtures of ethyl alcohol and water shows the rapid disappearance of the distinctive alcohol bands with increasing additions of water. Kohlrausch, Werner, and others have regarded hydration, or something of the sort, as a necessary part of the mechanism of dissociation in solution. A. A. Noyes has held somewhat analogous views.

Considering the work and ideas of all these investigators, together with the cation theory of catalysis, I am inclined, as a working basis, to combine these ideas in the following manner. From what has been said above it will be seen that all of the ideas are borrowed, but the combination may be suggestive. We will consider all, or practically all, hydrogen ions in water solution to be hydrated. From the great mobility of the hydrogen ion and from the work of Jones and Getman[1] on organic acids, the amount of water combined with this ion must be small, say, 1 H_2O, making $H_2\overset{+}{O}H$. In alcohol the hydrogen ion would be alcoholated forming, say, $C_2H_6\overset{+}{O}H$. In mixtures of water and alcohol some of the hydrogen ions would be hydrated and the others alcoholated. Since, as is shown by the work of Jones and Anderson, the tendency to hydration is much greater than the tendency to alcoholation, with equal numbers of water and alcohol molecules there would be more of the hydrated than of the alcoholated hydrogen ions. In the case of neodymium chloride in methyl alcohol and water, the tendency towards hydration appears to be about six times the tendency to alcoholation.

Bredig, Lapworth, Stieglitz, Acree, and others have adduced much evidence in favor of the view that it is the complex cation formed from the amide, acid, ester, etc., by the addition of the hydrogen ion which is the reactive compound. It makes no difference in the mathematical treatment of this idea or in any of the experimental work which has been

[1] This Journal, **32**, 455.

done to test this theory, whether we assume that the ion which is added to the base be $\overset{+}{H}$, $H_2O\overset{+}{H}$, or $C_2H_6O\overset{+}{H}$. But all the work on esterification, hydrolysis, etc., has gone to show that the reaction velocities are proportional to the concentrations of hydrogen ions as determined by conductivity, etc. The same conclusion was drawn concerning alcoholysis from the data in Table II. Hence it has been assumed by those who have worked on catalysis that the ions whose concentration is measured by electrical conductivity are the agents in catalysis, and that this is true whatever the medium, otherwise such close proportionality would not hold.

If the ion, $C_6H_5CONH_3\overset{+}{}$, is to react so as to give benzoic acid and ammonia it will have to come in contact with a water molecule to do so. It is simpler to assume that the hydrated hydrogen ion simply adds to the base,

$$C_6H_5CONH_2 + H_3\overset{+}{O} = C_6H_5CO_2NH_5\overset{+}{},$$

and that then this complex breaks up in course of time. It may break up into the very stable benzoic acid and ammonium ion,

$$C_6H_5CO_2NH_5\overset{+}{} = C_6H_5COOH + NH_4\overset{+}{}.$$

This is then the slow, monomolecular reaction. In the esterification of acids or amides the alcoholated hydrogen ion would add to the base in exactly the same way but these alcoholated complex ions would likely be even more unstable than the corresponding hydrated ions.

Mathematically, at least, it is necessary to assume the presence of at least a small number of $\overset{+}{H}$ ions. Then

$$[\overset{+}{H}] \times [H_2O] = K_{hy}\,[H_2O\overset{+}{H}] \text{ and } [\overset{+}{H}] \times [C_2H_6O] = K_{alc}[C_2H_6O\overset{+}{H}]$$

$$\text{and } \frac{[H_2O\overset{+}{H}]}{[C_2H_6O\overset{+}{H}]} = \frac{[H_2O]\,K_{alc.}}{[C_2H_6OK]\,K_{hy}} = h\,\frac{[H_2O]}{[C_2H_6O]}.$$

This is used in the discussion below.

There may be also an equilibrium between the $\overset{+}{H}$ ions and the free base. In this case the $\overset{+}{H}$ ions would be partitioned among the three bases, water and alcohol being considered as weak bases. Lapworth[1] has discussed mathematically the question of an acid in a mixture of such weak bases.

In a mixture of alcohol and water both processes would go on side by side. According to Lapworth's ideas the hydrated hydrogen ions are inactive in esterification, etc., and only insignificant amounts of nonhydrated hydrogen ions can be present in water solutions. In this connection, at least, he seems not to consider alcoholated hydrogen ions. If we accept this, it is not easy to see why there should be such close analogy between esterification of acids in alcohol and hydrolysis of amides in water. This analogy has been assumed and emphasized by Acree and others. The present work on alcoholysis serves to bring these even closer together. Besides, we have come to regard the hydrogen ions as they exist in water solution as extremely active.

In the case of an acid, say benzoic acid, in solution in a mixture of alcohol and water, the alcoholated hydrogen ions would combine with it to form complex ions, and so too may the hydrated hydrogen ions, and in even greater numbers. The complex alcoholated ions will break up, forming the ester, but when the hydrated ones break up they can only reform the benzoic acid. In the case of an acid and its ester both in the mixture of water and alcohol, both of these processes would go on with the acid and with the ester. When the ester combined with a hydrated hydrogen ion the complex ion could break up into acid and alcohol but when it combined with an alcoholated hydrogen ion, and the complex ion is decomposed, only ester can be formed. The effect will be to establish equilibrium, as is well known. Plainly the place to study the relative numbers and reactivity of these alcoholated and hydrated hydrogen ions is with such compounds as amides with which both can react. In the case of an amide in a mixture of water and alcohol, that is,

[1] *Loc. cit.*

in the presence of hydrated and alcoholated hydrogen ions, hydrated and alcoholated complex ions will be formed and each kind will decompose according to its own rate.

We may express these ideas in the following equations, the first of which are adapted from Lapworth. In these B stands for the amide or other base.

(1) $$B + C_2H_6O\overset{+}{H} = BC_2H_6O\overset{+}{H}.$$

(2) $$B + H_2O\overset{+}{H} = BH_2O\overset{+}{H}.$$

Then (3) $$[B] \times [C_2H_6O\overset{+}{H}] = \frac{1}{K'}[BC_2H_6O\overset{+}{H}]$$

and (4) $$[B] \times [H_2O\overset{+}{H}] = \frac{1}{K''}[BH_2O\overset{+}{H}].$$

Since it is the complexes, $BC_2H_6O\overset{+}{H}$ and $BH_2O\overset{+}{H}$, which are decomposing, each at a rate peculiar to itself, if V_a be the rate of alcoholysis and V_h the rate of hydrolysis, then

(5) $$V_a = [BC_2H_6O\overset{+}{H}]K_1,$$

and (6) $$V_h = [BH_2O\overset{+}{H}]K_2.$$

Substituting from (3) and (4) we get

(7) $$V_a = [B] \times [C_2H_6O\overset{+}{H}]K'K_1$$

and (8) $$V_h = [B] \times [H_2O\overset{+}{H}]K''K_2.$$

A number of different processes may be imagined by which the same complex ions may be ultimately formed. Several of these may be in operation at the same time. Quite a number of equations and equilibria may be written expressing these. These are linked together by the relation of the K's as mentioned below. The above was selected on account of its directness and simplicity.

The above equation states that the velocity of alcoholysis equals the concentration of the base multiplied by the concentration of the alcoholated hydrogen ion, and multiplied by two constants, one of which, K', represents the tendency of

the base to combine with the alcoholated hydrogen ion, and the other, K_1, the tendency of this complex cation to decompose. A similar statement may be made concerning the hydrolysis. The $[B]$ represents, of course, not the total amount of amide put into the solution but only so much of it as is present at any given time as the free base. It is not strictly correct to suppose that the same fraction of the amide would exist as free base in different solvents with different concentrations of acid, etc.

From Lapworth's work it appears[1] that $K' = \frac{K_4}{K_7 K_8}$ in which K_4 is the dissociation constant of the amidonium hydroxide, K_7 the hydration constant of the amide given by $K_7 = \frac{[Amide][H_2O]}{[Amide\ H_2O]}$ and K_8 the dissociation constant of water. K' is made up of a simlar set of values in which alcohol replaces water.

Unfortunately most of the data needed for detailed and accurate calculations are not known. Information is needed as to the dissociation constant for alcohol, the affinity constants of the amides, both in water and in alcohol, and their tendencies to form hydrates and alcoholates, also as to the relative hydration and alcoholation of the hydrogen ions, as well as more comprehensive data as to the degree of dissociation of hydrochloric acid in mixtures of alcohol and water at various temperatures. A knowledge of the influence of viscosity, osmotic pressure, heats of dilution, etc., on reaction velocities is also required.

Acree and Nirdlinger[2] concluded that in somewhat similar concentrations, not over 4 per cent of the acetamide was present as salt in water solution. If the amount of salt formed in alcoholic solution is not greatly different, for an approximate calculation we may consider $[B]$ to have the same value in the two equations (7) and (8). From the data of Kablukoff as above discussed, it appears that at $V = 1$, hydrochloric acid in alcohol is dissociated 37 per cent, while in water, at the same volume, the dissociation is 78 per cent. Hence

[1] J. Chem. Soc., **93**, 2166.
[2] *Loc. cit.*

if we assume, as above, that all ions are alcoholated in alcohol and hydrated in water, for pure alcohol we will have for 1 N HCl $[C_2H_6\overset{+}{O}H] = 0.37$, and for pure water and 1 N HCl, $[H_2\overset{+}{O}H] = 0.78$. Green[1] has concluded that the mobility of the ions, in conductivity, varies inversely as the two-thirds power of the viscosity. Assuming, for the present, that the same relation holds as to reaction velocities, 296, the alcoholysis velocity found for benzamide, has been multiplied by $\left(\frac{0.00957}{0.00590}\right)^{2/3}$, 0.00957 being the viscosity of the solution in which the alcoholysis velocity was measured and 0.00590, that of the corresponding water solution in which the hydrolysis velocity was measured. This gives 408, which is assumed to be the rate at which alcoholysis would take place in a solution of the same viscosity as that in which the hydrolysis was measured. I intend measuring the effect of the viscosity of the medium on a number of these reactions, so as to have a sure basis for such calculations as this.

Then $\quad 408 = [B] \times 0.37 \times K_1K'$
and $\quad 234 = [B] \times 0.78 \times K_2K''$.

Taking $[B]$ as practically equal to 1 in each case, we get $K_1K' = 1103$, and $K_2K'' = 300$. These are then the velocities with which alcoholysis and hydrolysis might be supposed to take place in solutions of equal fluidity and with 100 per cent dissociation of the hydrochloric acid. They are relative, rather than absolute. Assume that the hydration tendency is h times as great as the alcoholation tendency. Then in the alcohol of Series X., in which there were 86.1 molecules of alcohol to 13.9 of water, the relative number of alcoholated and hydrated hydrogen ions would be 86.1×1 and $13.9 \times h$. Putting these in the formulae above we have

$$V_a = [B] \times a \times 86.1 \times 1103$$
and $$V_h = [B] \times a \times 13.9h \times 300.$$

Since in a given solution at a given time $[B]$, the concentration of the amide, and a, the per cent of dissociation of the

[1] J. Chem. Soc., **93**, 2049.

acid, have the same pair of values in the two equations, the relative rates of alcoholysis and hydrolysis may be obtained from these by division. But this ratio was measured and found to be 7.9 in this series, and 4.6 in Series XI. Equating these values, $7.9 = \frac{1103 \times 86.1 \times 1}{300 \times 13.9 \times h}$, $4.6 = \frac{1103 \times 75.5 \times 1}{300 \times 24.5 \times h}$. From these h comes out 2.9 for the first, and 2.5 for the second. This is intended to be simply suggestive of a line of approach.

I intend to take up this subject in a comprehensive way and by a study of these and other amides in a variety of mixtures and concentrations, I hope to accumulate data which will aid in the solution of these questions.

In returning, after ten years, to the hydrolysis of acid amides, on which I worked several years, first under President Remsen[1] and later independently,[2] I have taken up the subject with the additional light which has been thrown on the mechanism of this and other analogous reactions by the modern theories of Kastle, Euler, Bredig, Acree, Stieglitz, Goldschmidt, Lapworth and others. This has been done by arrangement with Professor Acree who was the first to study amides from the newer point of view. The alcoholysis of the amides has come up as a development of my work on hydrolysis of amides, on which I hope to report later.

JOHNS HOPKINS UNIVERSITY,
BALTIMORE, MD.,
April 7, 1909.

[Contributions from the Laboratory of Harvard College.]

AN APPARATUS FOR THE EXTRACTION OF LIQUIDS WITH ETHER.

BY AUGUSTUS H. FISKE.

For the purpose of extracting solutions with ether, or other low-boiling liquids, it has been customary in this laboratory, to use a simplified form of the apparatus of Van Rijn,[3] but, since the liquid to be extracted is contained in a tall, narrow

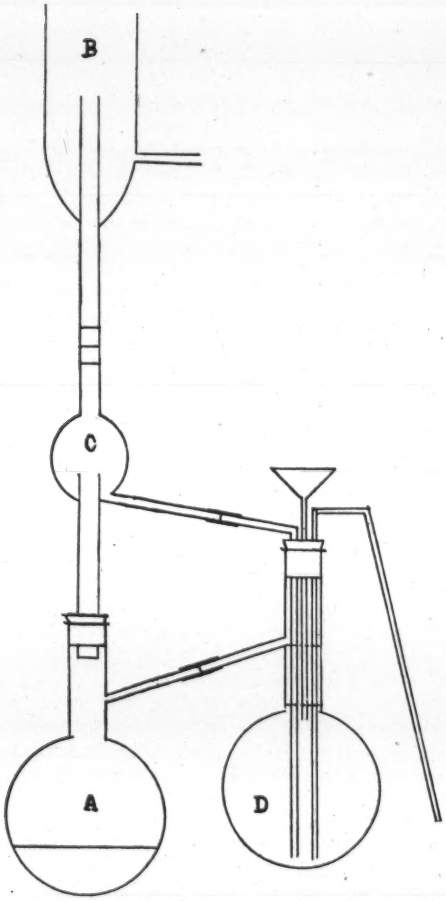
[1] THIS JOURNAL, **21**, 281.
[2] *Ibid.*, **24**, 397.
[3] Ber. d. chem Ges., **28**, 2387 (1895).

vessel inside the jacket which conducts the hot vapors to the condenser, the amount which may be extracted at one time is limited by the size of the jacket to 150 or 200 cc. Having occasion to extract a liter or so of solution at a time, the following apparatus was devised, which is simpler and more efficient than any of the other extraction devices already described, so far as I can find.

The apparatus consists of a flask (A) above which is a reflux condenser (B), but between the lower end of the condenser and the flask is inserted a trap (C), from which the distillate is conducted to the flask (D) containing the solution to be extracted. The trap (C) consists of a small bulb at the mouth of the condenser tube, which catches the distillate as it runs down the walls of the tube, and draws it off without allowing it to run back into the distilling flask below. This trap is a modification of the apparatus of Boessneck,[1] which, however, requires such a large tube for the condenser that its efficiency is much impaired, and the cork over which the extracting liquid runs is a source of contamination. The last mentioned disadvantage appears as well in the apparatus of Eiloart,[2] while in the extractor of Shenstone,[3] which is less closely related to the form here described, the diameter of the condenser tube is much reduced by the gutter placed about the inner wall, and this forms a serious obstacle to the free passage of vapors from the distilling flask to the condenser. It would also appear to be a very difficult piece of apparatus to construct. In the apparatus shown, the common laboratory condenser is used, the stem of the trap being connected to the condenser by a piece of rubber connecting tubing.

The flask (D) is a common distilling flask of 500 cc. or a liter capacity, containing the solution to be extracted. The extracting solvent is led from the drain of the trap to the bottom of (D), passes up through the liquid, and then runs back through the side tube of (D) to the distilling flask (A) to be distilled again. To obviate the necessity of taking the apparatus to pieces when the liquid in (D) is to be renewed, a siphon is

[1] Chem. Ztg., **14**, 870 (1890).
[2] Chem. News, **53**, 281 (1886).
[3] J. Chem. Soc., **1883**, 125.


B
C
A
D

provided to draw off the spent liquid, and a funnel for refilling. The stem of the funnel should be long enough to dip below the surface of the liquid in (D), to prevent the escape of any vapor which may find its way up the side tube from (A).

To find the relative efficiency of the apparatus, solutions of succinic acid in water were extracted with ether in it and in the Van Rijn apparatus under approximately the same conditions, and for the same length of time. After allowing the apparatus to act for 2½ hours, in each case, the following results were obtained. The Van Rijn apparatus, holding 125 cc. of a solution containing 5.7 per cent solid succinic acid, extracted 62 per cent of the substance. The new extractor, holding 540 cc. of a solution containing 6.4 per cent solid succinic acid, extracted 67 per cent of the substance. These results were obtained under the usual conditions of work in the laboratory, and although only rough determinations, they show conclusively, that the new form of apparatus, is just as efficient, per cc. of solution extracted, as the older form, while it will extract 4 times as much solution in the same length of time. Undoubtedly the flask (D) might be increased in size to hold larger volumes of solution, without impairing the efficiency of the apparatus. There must be a limit, however, to the diameter of the flask which may be used, and still allow the extractor to work efficiently, but on reaching this limit, if still larger volumes of liquid are to be extracted, the increase in size must come in a vertical direction. The neck of the flask is a distinct advantage here, as it permits the existence of a sufficient layer of ether above the solution, without necessitating the use of a large excess which takes no active part in the work of extracting. A cylindrical vessel, therefore, should be used, which should have a neck with a side tube like a distilling flask. Neumann,[1] Eiloart,[2] Diepolder,[3] and Foerster,[4] have described cylindrical containers for the liquid to be extracted in their forms of the apparatus, but without the neck and side tube.

[1] Ber. d. chem. Ges., **18,** 3061 (1885).
[2] Chem. News, **53,** 281 (1886).
[3] Ber. d. chem. Ges., **30,** 1797 (1897).
[4] Chem. Ztg., **22,** 421 (1898).

To extract solutions of high specific gravity, the vertical difference between (C) and the level of the ether in (D) may not be enough to allow an ether column of sufficient height to force its way down the delivery tube of (C), through the heavy liquid in (D). If this is the case, the vertical distance from (A) to (C) should be increased until the column of ether in the delivery tube is sufficiently heavy to start the circulation. In the Van Rijn apparatus, it is impossible to increase the height of the ether column without reconstructing the entire apparatus. Therefore, to extract heavy solutions in this device, it is necessary to reduce the quantity of the solution, in order to get a satisfactory circulation of ether through the liquid; but in reducing the vertical height of the solution, you reduce the proportional amount of solution with which the ether comes in contact and likewise, the length of time in which the ether is in contact with the substance to be extracted. Thus the ether will have less chance to become saturated with it.

The ideal form of extractor would be one in which the length of solution through which the ether passes is sufficient to allow the ether to take up its greatest content of extractive substance, but as it takes some time for the ether to come into equilibrium with the solution, this equilibrium point is probably never approached in any extractor of this character. Therefore, it follows that the longer the ether may be in contact with the solution, the more efficient is the action of the extractor, other conditions remaining the same. As the action of the extractor depends on the relative solubility in water and ether of the substance to be extracted, then, for every individual substance, there is a different degree of saturation of the ether during the extraction, and at the same time, this equilibrium changes as the solution which is to be extracted becomes more dilute. From these considerations we can see that there can be no general rule for the height of solution to be extracted, but in order to have the extractor do its best work, we should make the solution as deep as we can, which would force the ether to come in contact with as much solution as possible, and simultaneously make it stay

in contact with the solution the greatest possible length of time. The reduction of the height of the column of solution in the Van Rijn apparatus is, therefore, very detrimental to its efficient action.

The trap (C) may also be used for the ordinary distillation of liquids, where economy of space on the laboratory desk is required. When using the trap for this purpose, a small U-shaped bend should be made in the delivery tube to form a liquid seal, thereby preventing the escape of uncondensed vapors in this direction. Various devices for distillation have been proposed by Wollney,[1] Leather,[2] Peters and Rost,[3] and Chatelan,[4] but all are more complex than the trap described above.

CAMBRIDGE, MASS.,
March 19, 1909.

RADIOACTIVITY.[5]

BY W. MARCKWALD.

1. Electricity in Gases.

The first suggestion of an atomic conception of electricity was furnished by Faraday's law of electrolysis, for this law found its obvious explanation in the assumption that each valence of an ion combined with the same elementary quantity of electricity. This quantity, usually denoted by ε, could be calculated and was found to be 3.2×10^{-10} electrostatic units.[6] But only with the recent discoveries as to the electric behavior of gases was a firm foundation given to this hypothesis. As is well known, gases are usually nonconductors of electricity, or at any rate it is not proved that they are ionized when unaffected by exterior influences, but they become so when acted on by light of short wave length (ultraviolet light), or when subjected to high temperature, to Röntgen rays, or to other

[1] Z. anal. Chem., **24**, 56 (1885).
[2] J. Soc. Chem. Ind., **8**, 81 (1889).
[3] Z. angew. Chem., **1896**, 485.
[4] Chem. Ztg., **25**, 612 (1901).
[5] Address delivered before the German Chemical Society, May 2, 1908, and published in Ber. d. chem. Ges., **41**, 1524. Translated by B. B. TURNER.
[6] Stoney: Belfast Meeting, Brit. Ass., **1874**. Richarz: Wied. Ann., **52**, 385 (1894).

rays which will be mentioned later. Under these circumstances the gaseous ions are driven by an electric field towards the electrodes in opposite directions with a velocity which depends chiefly on the potential difference. If this is increased, the current also increases up to a certain point, and then remains constant. The maximum current is called the "saturation current," which is a measure of the ionizing power of the rays that are acting. Theoretically, this phenomenon is explained by assuming that when the rays fall on the atoms of the gas, these give off negatively charged elementary particles, electrons, which, as well as the positively charged atoms that are left, combine with neutral molecules to form large ionic-molecular aggregates. This hypothesis explains the comparatively slow rate of diffusion of the gaseous ions,[1] as a consequence of which the ions do not move fast enough in a weak electric field to reach the electrodes before a number of them have been neutralized by oppositely charged ions. When the potential difference is high enough, however, practically all the ions reach the electrodes and the strength of the current depends solely on the source of energy which brings about the formation of new ions.

Townsend,[2] J. J. Thomson,[3] and others have measured experimentally the electric charge carried by each ion of gas, and found that the value of ε for any gas is almost identical with that for the hydrogen ion in solution, a fact whose importance for the hypothesis of electrons is obvious. However, according to Townsend's latest investigations,[4] this holds only for the negative ion, the positive ions of a gas carrying a double charge, which would imply also the splitting off of two electrons by each atom of gas.

The electric properties of gases undergo a radical change when subjected to high potential discharges at very low pressures, as in the so-called Hittorf's or Crookes's tubes. There are then expelled in straight lines from the cathode at enormous velocities corpuscles, which, before the discovery that

[1] Riecke: Ann. Phys. [4], **12**, 74 (1903).
[2] Phil. Mag. [5], **45**, 125 (1898). Phil. Trans., **193**, A, 129 (1899).
[3] Phil. Mag. [5], **46**, 528 (1898); **48**, 557 (1899); [6], **5**, 346 (1903).
[4] P. Roy. Soc., **80**, A, 207 (1908).

this was not a case of real radiation, were named cathode rays. These corpuscles are deflected both by electric and magnetic fields, and the direction in which they are deflected indicates that they carry a negative charge. From the amount of the deflection Wiechert,[1] J. J. Thomson,[2] and others were able to calculate the velocity and also the ratio ε/μ of charge to mass. The former is, on the average, about 1/10 the velocity of light, though Lenard, in his well known experiment, has been able, by passing the rays through an aluminium window, to filter out rays of greater penetrating power and having a velocity ¼ that of light. The ratio ε/μ is independent of the nature of the gas in the tube, and is likewise practically constant for rays of average velocity, amounting to about 1.8×10^7 in electromagnetic units, while the ratio ε/μ for the electrolytic hydrogen atom is approximately 10^4.

If we make the assumption, which has been established by Thomson in a way that we cannot now go into, that the charge carried by the corpuscles is equal to the atomic charge of gases under atmospheric pressure, and therefore, as we saw, equal also to the charge carried by the hydrogen ion in solution, the mass of the corpuscles is found to be about 1/1800 of that of the hydrogen atoms. Furthermore, Thomson holds that even this mass is not real, assuming rather that the corpuscles of the cathode rays, that is, the electrons, only show an apparent mass because they must possess a certain amount of inertia, in consequence of the attraction exerted by the surrounding ether. It can be calculated mathematically that the resistance to change of motion which the electron must experience as a result of this inertia will be appreciably constant as long as the velocity remains within the limits so far observed in the case of cathode rays, but that it must increase as the velocity approaches that of light, and would become infinitely great, and therefore the electron would appear to have an infinite mass, when this limit is reached. We shall find an important confirmation of this hypothesis when we come to consider the rays from radium.

[1] Abhdlg. phys.-ökon. Ges. Königsberg, **38**, 1 (1897); Wied. Ann., **69**, 739 (1899).
[2] Phil. Mag. [5], **44**, 293 (1897); **48**, 547 (1899).

If then the process of ionization is regarded as the separation of an electron from the atom, and if the electron is admitted to have an apparent mass, we are naturally led to regard the residual atom also as an aggregation of electrons. The explanation of the Zeemann effect and of the periodic system of Mendeléeff and Lothar Meyer furnished by this hypothesis can only be referred to here.

Besides the cathode rays, Goldstein discovered in the discharge through a vacuum tube another kind of radiation known as "canal rays." These travel in a direction opposite to that followed by the former rays and are oppositely deflected by magnetic and electric fields.[1] It follows that we have to do here with positively charged particles. Their velocity is only slightly less than that of the cathode rays, but their mass, as calculated from the ratio ε/μ on the hypothesis that each particle of the canal rays carries only one electric charge, is of the order of magnitude of the atoms.

A third kind of radiation outside the vacuum tube has been demonstrated by Röntgen. These rays, named after the discoverer, are produced, together with heat and light, when the cathode rays strike an obstacle. We are inclined to consider them as wavelike motions in the ether, because they are not deflected by magnetic nor by electrostatic forces.

II. The Discovery of Uranium Rays.

When the cathode rays strike the glass wall of a vacuum tube, a brilliant fluorescence is excited. Accordingly, shortly after the discovery of the Röntgen rays, Poincaré suggested that this fluorescence might be the source of the new rays, and that possibly all fluorescent substances emitted similar rays. This induced Becquerel[2] in the year 1898 to investigate the action of the beautifully fluorescent uranium salts, uranium potassium sulphate, for example, on the photographic plate. He found, in fact, that the salts affected the plates through light-proof paper, just like the Röntgen rays. However, the same photographic effect was

[1] W. Wien: Verh. physik. Ges., **16**, 165 (1897); **17**, 10 (1898).
[2] Compt. rend., **122**, 420, 501, 559, 689, 762, 1086 (1896).

also observed when the fluorescent salts were replaced by other uranium compounds, and the effect was strongest with metallic uranium itself. As other phosphorescent substances did not affect the plates through an opaque material, Becquerel came to the conclusion that the radiation observed is characteristic of uranium and its compouuds.

The uranium rays, like the Röntgen rays, ionize gases. Being able, as we have seen, to measure quantitatively the ionizing power of such rays by means of the saturation current, as indicated by a suitable electrometer, Mme. S. Curie[1] compared the action of equal quantities of different uranium compounds distributed over equal surfaces and found it approximately proportional to the uranium content, from which she concluded that the radiation is a property of the uranium atom. This, with a certain reservation, is still held to be true at the present day.

Of the remaining elements known up to the year 1898, only one showed "radioactivity," namely, thorium, the radiating power of which was discovered almost simultaneously by C. G. Schmidt[2] and S. Curie,[3] and found to be of the same order of magnitude as that of uranium.

III. Radium and Polonium.

So much the more striking was it, therefore, that uranium minerals, as Mme. Curie found in one of her researches, showed an unexpectedly high activity. Thus pitchblende from Joachimsthal, the most important raw material in the uranium industry, though containing only about 50 per cent of uranium, surpassed this metal threefold in activity. This observation led M. and Mme. Curie to the supposition that the mineral might contain an unknown substance, with a radioactivity much greater than that of uranium. A complete analytical investigation of the pitchblende, in which each fraction separated was tested with the electrometer, confirmed this view. The bismuth which was present in the mineral to the extent of about 0.3 per cent was found

[1] Ann. chim. phys. [7], **30**, 99 (1903).
[2] Wied. Ann., **65**, 141 (1898).
[3] Compt. rend., **126**, 1101 (1898).

to be almost 100 times as active as uranium, and as ordinary bismuth is inactive, an element, unknown till then, must have been mixed with the bismuth separated from the pitchblende. The separation of this element was next undertaken, at first with very little success. The name given to it by its discoverers was polonium.[1]

In the further investigation of pitchblende, in which Bémont took part, P. and S. Curie[2] found a second very active constituent. The barium, which was precipitated in still smaller amount than the bismuth, showed about the same activity, and in this case, by means of fractional crystallization of the chloride, they succeeded in accumulating the active constituent, to which they gave the name radium, in the first fractions, and thus eventually they obtained pure radium chloride.

But before this end could be attained, many tons of the uranium ore had to be worked up. This substance is treated at the Joachimsthal mine with sulphuric acid with the addition of a little nitric acid, and the uranium salt is extracted. There remains a residue amounting to about 1/3 of the original ore, consisting chiefly of gangue, but containing also lead, copper, iron, bismuth, and other salts, among which is a very small amount of barium-radium sulphate. To separate this, the entire mass is first boiled with alkali, to decompose the sulphates. Silica and plumbic hydroxide go into solution at the same time. The residue from the treatment with alkali is extracted with hydrochloric acid to dissolve the oxides of the heavy metals and the earths. The undissolved portion is now boiled with concentrated sodium carbonate solution to convert the sulphates of barium and radium into carbonates, the liquor is carefully removed by washing, and the residue is extracted with hydrochloric acid free from sulphuric acid. The mixture of barium and radium salts is thus brought into solution and purified by the analytical methods customary in the case of barium. In this way, from a ton of Joachimsthal residues, there are obtained 3–4 kilograms of barium-radium sulphate, containing at most 0.4 gram of radium. An analytical method

[1] Compt. rend., **127**, 175 (1898).
[2] *Ibid.*, **127**, 1225 (1898).

for separating radium from barium by chemical reagents has not yet been discovered, and the preparation of pure radium salts has been achieved only by fractional crystallization of their salts. The corresponding salts of radium and barium seem to give mixed crystals in all cases, so that only by a complicated process of fractionation can the desired end be reached. According to Giesel,[1] the separation is effected most easily through the bromides.

The spark spectrum of radium has been thoroughly investigated by Demarçay,[2] Runge and Precht,[3] and others. Three very bright lines are conspicuous in the blue and violet. The flame spectrum, described by Giesel,[4] is characterized by two red bands, so that the flame of the Bunsen burner is colored intensely carmine-red by radium salts.

The atomic weight of radium has been determined by Mme. Curie[5] from the proportion of chlorine in the chloride, and in the earlier investigation, carried out with only 0.1 gram of the salt, was found, on the assumption that the formula for the chloride is $RaCl_2$, to be 225. In her later determination with 0.4 gram at her disposal, she obtained the value 226.18.

The radiating power of pure radium salts surpasses that of uranium more than a millionfold. The surprising effects which a few milligrams of these salts can produce have greatly increased popular interest in the discovery of radioactive substances. The discharge of an electroscope is effected almost instantaneously at a great distance; phosphorescent substances, as barium platinocyanide, zinc blende, diamond, willemite, and many others, are made brilliantly luminous, and the radium salts themselves phosphoresce. Many other substances, among which nitrogen and helium[6] are especially interesting, show a certain degree of phosphorescence, when subjected to the action of radium.

The photochemical effect of radium can be detected at a

[1] Wied. Ann., **69,** 91 (1899).
[2] Compt. rend., **127,** 1218 (1898); **129,** 116 (1899); **131,** 258 (1900).
[3] Ann. Phys. [4], **10,** 655 (1903); **12,** 407 (1903).
[4] Ber. d. chem. Ges., **35,** 3608 (1902).
[5] Compt. rend., **135,** 161 (1902); **145,** 422 (1907).
[6] Sir William and Lady Huggins: P. Roy. Soc., **72,** 169, 409 (1903); **76,** 488 (1905); **77,** 130 (1905). Himstedt and Meyer: Physik. Z., **6,** 688 (1905); **7,** 762 (1906).

distance of as much as 2 meters, but by long exposure much more powerful effects than that on the photographic plate are caused by these rays. Glass is colored violet or gray according to its composition. Giesel[1] has shown that the salts of the alkalies acquire the same color as Goldstein has produced in them by the action of cathode rays; common salt is colored brown, potassium chloride violet, and potassium sulphate green. Many reactions are catalytically accelerated by the radium rays, such as the formation of hydrogen chloride[2] from its elements, for instance, and the decomposition of hydrogen peroxide.[3] Air in contact with radium bromide is ozonized, a change with which is associated an interesting oxidation of the salt to hypobromite, and its conversion into carbonate under the influence of the carbon dioxide of the air.[4] From an aqueous solution of radium bromide small quantities of hydrogen and oxygen are evolved continuously, and there is always more hydrogen in the mixture than corresponds to the composition of water.[5] This fact has yet to be explained, as it has not been possible to demonstrate any accompanying oxidizing action which would account for the loss of oxygen.

The physiological action of the radium rays, which resembles very closely that of the Röntgen rays, was noticed first by Walkhoff,[6] and soon confirmed by Giesel,[7] and also by Becquerel and P. Curie.[8] If the skin is exposed for a long time to the rays, blisters and even penetrating ulcers are formed. This, and the bactericidal action discovered by Aschkinass and Caspari,[9] have led to attempts to utilize the rays therapeutically, but so far such attempts have met with doubtful success.

The energy evolved by radium was first measured calorimetrically by P. Curie and Laborde,[10] who found that 1 gram

[1] Verh. d. physik. Ges., Jan., **1900**.

[2] Jorissen and Ringer: Ber. d. chem. Ges., **38,** 899 (1905); Arch. néerland. sci. exact. nat. [2], **12,** 157 (1907).

[3] Fenton: P. Camb. Phil. Soc., **12,** 424 (1904).

[4] P. and S. Curie: Compt. rend., **129,** 823 (1899).

[5] Giesel and Bodländer: Ber. d. chem. Ges., **36,** 347 (1903). Ramsay and Soddy: P. Roy. Soc., **72,** 204 (1903). Ramsay: J. Chem. Soc., **91,** 931 (1907).

[6] Photogr. Rundschau, Oct., **1900**.

[7] Ber. d. chem. Ges., **33,** 3569.

[8] Compt. rend., **132,** 1289 (1901).

[9] Arch. physiol. Ges., **86,** 603 (1901).

[10] Compt. rend., **136,** 673 (1903).

of radium liberates in 1 hour 100 calories. According to Ångström[1] the correct value for the heat evolved is greater, namely, 117 cal., while Precht[2] obtained a still greater value, 134.4 cal. Such an evolution of heat is sufficient, as Giesel[3] has shown, to maintain the temperature in a flask containing 0.7 gram radium 5° C. above that of the surrounding medium.

In the year 1902 polonium[4] was first separated from pitchblende. Electrolytic experiments showed that the metal is far more "noble" than bismuth, so that their difference in solution tension is enough to cause the deposition of polonium on a rod of bismuth dipped in a solution of the chloride. Stronger reducing agents, such as stannous chloride, for example, precipitate it from its solution. The precipitate, which amounts to about 0.3 part per thousand of the bismuth present, consists chiefly of tellurium, from which the polonium can be separated in various ways, the most convenient being the precipitation, by excess of ammonium hydroxide, of the polonium as hydroxide from the solution of the chlorides acidified with hydrochloric acid, or the precipitation of the tellurium by hydrazine. Starting with 50 kilograms of bismuth from 15 tons of pitchblende, a nearly quantitative yield of 3 milligrams of the substance, which was certainly still impure, was obtained. These figures show that the quantity of polonium in the bismuth from pitchblende is less than that of radium in the pitchblende itself.

That these elements could be found at all is solely due to their radiating power, and the manner of their discovery reminds one strongly of the discovery of the rare alkali metals by Bunsen and Kirchoff by means of spectrum analysis. But the electrometer test for radium is a million times more sensitive than the spectroscopic test, although the spectrum of the element is very characteristic, and the radioactivity of polonium is a thousand times greater than that of radium. To give an idea of the delicacy of the electrometric method, we may

[1] Physik. Z., **6**, 685 (1905).
[2] Ann. Phys. [4], **21**, 595 (1906).
[3] Ber. d. chem. Ges., **36**, 2370 (1903).
[4] W. Marckwald: Ber. d. chem. Ges., **35**, 2285, 4239 (1902); **36**, 2662 (1903) **38**, 591 (1905).

imagine the above 3 milligrams of polonium electrolytically deposited on a copper band the length of the equator; then if a piece of this band 1 cm. long, that is, a 4000-millionth part were taken, its radioactivity could be detected easily with the electroscope.

A method for the separation of polonium was indicated by the periodic system, which showed a gap after tellurium in the sixth group for an element of atomic weight 210. The hypothesis that polonium belonged in this place was the means of foreseeing its chemical properties, and finding a way to separate the new element from the old.

The following figures on the separation of new elements from great dilutions are of some interest:

1 part caesium was separated from 6 million parts Dürkheim water,

1 part xenon was separated from 40 million parts air,

1 part radium was separated from 10 million parts pitchblende,

1 part polonium was separated from 5000 million parts pitchblende.

IV. Rays from Radioactive Substances.

The rays emitted by radium and polonium differ in a characteristic manner. As early as 1899 Rutherford[1] showed that the rays from uranium are complex in their character. Some of them, the α-rays, have slight penetrating power and are stopped by a sheet of aluminium 1/10 mm. thick, and since they are likewise absorbed by gases to a corresponding degree they have a strong ionizing action. The rest, the β-rays, have about 100 times as great a power of penetration, and show, in consequence, proportionally less ionizing action. Still another kind of rays, present in very much smaller proportion, the γ-rays, were demonstrated later by Villard.[2] These rays are about 100 times more penetrating still than the β-rays. Radium, uranium, and thorium emit all three kinds of rays, while polonium gives off, leaving out of account, for the present, the newly discovered δ-rays, only α-rays.

The explanation of the nature of these rays is furnished by

[1] Phil. Mag. [5], **47**, 109 (1899).
[2] Compt. rend., **130**, 1010 (1900).

their behavior in magnetic and electric fields. Giesel[1] and also St. Meyer and von Schweidler[2] were the first to show that the β-rays are deflected by a magnet in the same way as the cathode rays, and by measuring the magnetic and electrostatic deflections, Becquerel[3] showed that the β-rays from radium must be considered as cathode rays of very variable velocity. While the slower rays are about equal in velocity to those produced in a vacuum tube the fastest, and therefore most penetrating, rays have almost the velocity of light. In the case of the latter Kaufmann[4] has determined the ratio ε/μ of electric charge to mass, and found that the deduction from Thomson's electron hypothesis, that, as we saw, the apparent mass of the electrons must increase with their velocity, is confirmed by the facts.

The α-rays resemble the canal rays to the extent that their deflection by magnetic and electric fields shows them to be positively charged particles of atomic dimensions. Rutherford[5] determined their velocity and found this to be constant for each individual radioactive substance; in the case of different substances the velocity varies, as far as determined experimentally, between 1/20 and 1/13 of that of light. On the other hand, the ratio ε/μ is the same for all substances. It amounts to 5.07×10^3 and is therefore almost exactly half as great as in the case of the hydrogen ion. The particles must therefore be at least twice as great as the hydrogen atom, if we assume the indivisibility of the electric charge. Rutherford has put forward the hypothesis that the α-particles are helium atoms which carry two electric charges, or, otherwise expressed, have lost two electrons.

The charge of the α-rays proceeding from any source can be measured electrometrically by receiving them on a metal plate in a vacuum. As the charge of the individual α-particles is known, the number of particles emitted in unit time can be ascertained. By further determining the saturation current

[1] Wied. Ann., **69**, 831 (1899).
[2] Physik. Z., **1**, 90 (1899).
[3] Compt. rend., **130**, 206, 372, 810 (1900).
[4] Nachr. k. Ges. Wiss. Gött., **1900**, No. 2.
[5] Physik. Z., **4**, 235 (1902); Phil. Mag. [6], **12**, 348 (1906); **13**, 110 (1907).

which they produce in air, the number of pairs of ions produced by one particle can be determined.[1] This is dependent upon the velocity of the rays and, assuming that each particle carries two charges, it amounts on the average to 200,000. Quite recently Regner[2] has applied an interesting method to the problem of counting directly the particles emitted by polonium. For this purpose he made use of a phenomenon discovered by Crookes.[3] While, in general, phosphorescent substances are thrown into a state of uniform luminescence by the α-rays, as also by all similar rays, a screen of Sidot's blende, especially when examined with a lens, shows a characteristic play of sparks. Crookes explained this behavior as caused by a bombardment by the α-particles. Regner brought under the microscope a feeble polonium preparation with a screen of zinc blende in such a manner that he could count the separate flashes of light. From the saturation current produced by the same preparation he calculated the number of particles emitted, and assuming that each particle carried two charges he found in this manner numbers which agreed with sufficient accuracy.

In penetrating any medium the velocity of the α-rays is reduced without any change taking place in the proportion of charge to mass and the reduction is proportional to the square root of the thickness of the layer penetrated.[4] When the velocity has sunk to about $1/36$ of the velocity of light the rays suddenly lose their power of ionizing gases, of causing phosphorescence, and of acting on the photographic plate. We have then no means whatever of ascertaining their presence; and since, moreover, the velocity of the rays emitted is, as we saw, different for different radioactive elements, it follows that the limit of their activity in air must be characteristic of each substance. For polonium, the range of activity in air under normal circumstances amounts to 3.86 cm.[5] Bragg and Kleemann[6] have shown that by means of this character-

[1] Rutherford: Phil. Mag. [6], **10**, 207 (1905).
[2] Verh. d. physik. Ges., **10**, 78 (1908).
[3] Chem. News, **87**, 241 (1903.)
[4] Rutherford: Phil. Mag. [6], **12**, 134 (1906).
[5] Levin: Physik. Z., **7**, 513 (1906).
[6] Phil. Mag. [6], **8**, 917 (1905); **10**, 318 (1906).

istic not only can the individual radioactive elements be identified in a simple manner but mixtures can also be analyzed without further trouble.

The γ-rays have been as yet comparatively little studied. They form only a small fraction of the energy emitted by radium. As they are not deflected magnetically nor electrostatically, they resemble the Röntgen rays, especially such as are produced from "hard" tubes.[1] McClelland[2] and Wiggers[3] have shown that they are not homogeneous.

That the β-rays from radium carry electric charges may be shown by a pretty experiment which was devised by Strutt.[4] A small glass tube containing radium salts is hung in an exhausted vessel and well insulated. The exterior walls of the tube are made capable of conducting by being painted with phosphoric acid, and two leaflets of aluminium are fastened to them; the negatively charged β-rays penetrate the walls of the tube, while the positively charged α-particles are kept back, whereby a positive charge is produced in the interior of the tube, and transferred by induction to the outer walls. The aluminium leaflets diverge until they touch the walls of the vacuum vessel, which are connected to the earth, when they are discharged, collapse, and the occurrence is repeated.

If polonium emitted only α-particles it would acquire *in vacuo* a negative charge, but J. J. Thomson[5] has shown that the contrary is the case. He finds the explanation in the fact that besides the α-rays there is present another kind of very slow, easily absorbed β-rays which have been called δ-rays. Their velocity is only about 1/100 of that of light,[6] so that they can be so strongly deflected by a magnetic field that they will return in a circular path to the point from which they started. As the α-particles experience only a slight deflection it follows that in a magnetic field polonium will acquire a negative charge.

[1] Eve: Phil. Mag. [6], **8**, 610 (1904).
[2] *Ibid.* [6], **8**, 70 (1904).
[3] Z. Radioakt., **2**, 420 (1905).
[4] Phil. Mag. [6], **6**, 588 (1903).
[5] Nature, **71**, 438 (1905).
[6] Ewers: Physik. Z., **7**, 148 (1906).

V. The Hypothesis of Disintegration: Uranium and Uranium X.

Since the discovery of radioactivity, the question has been vigorously discussed as to how the new phenomena are to be brought into line with the law of conservation of energy. Numerous hypotheses were put forward to explain how radium could apparently give out its rays continuously without ever becoming exhausted and without receiving any demonstrable accession of energy from without, but none of these were satisfactory, nor did any of them further our knowledge of the nature of radioactivity. But at the end of the year 1902 Rutherford and Soddy[1] came forward with their hypothesis of the breaking down of the atoms of radioactive elements and so brought clarity into the apparently confusing abundance of contradictory observations. This hypothesis has in the meantime been so brilliantly confirmed by new experiments, of the accumulation of which it has often been the inciting cause, that its rapid success is probably unexampled in the history of science. It will therefore be well to discuss in connection with this hypothesis the development which the investigation of the radioactive phenomena has gone through in the last five years. But first let us consider the most important facts which have led to its formulation.

While the dependence of the activity of the various uranium compounds on their content of uranium made it natural to suppose that the radiation is a characteristic of the uranium atom, one observation by Crookes[2] seemed to contradict this. He was able to separate from uranium an exceedingly small quantity of a substance which acted very vigorously on the photographic plate, while the uranium that remained had lost this power. Crookes named this substance uranium X. For its separation several methods were used. If uranium nitrate containing water of crystallization is dissolved in ether an ethereal solution of the anhydrous nitrate and an aqueous layer which contains but very little dissolved salt are obtained. The whole of the uranium X is found in the aqueous solution, together with a small quantity of uranium nitrate. Another method

[1] Phil. Mag. [6], **4**, 370, 569 (1902); **5**, 576 (1903).
[2] P. Roy. Soc., **66**, 409 (1900).

for separating uranium X from uranium consists in treating the solution of uranium salt with an excess of ammonium carbonate, in which, as is well known, the precipitate first formed redissolves. The uranium X is then precipitated, together with the other impurities of the uranium, such as iron. If the original uranium salt is very pure, small quantities of impurities must be added to it to produce the precipitate.

Becquerel[1] found another way to separate uranium X from uranium, and made the more important observation that the former lost its activity in the course of a few months, while the latter regained its original activity in the same time. He could then repeat the process of separation of the active constituent as often as he pleased.

These observations were extended and corrected in an important particular by Soddy,[2] as well as by Rutherford and Grier.[3] Crookes and Becquerel had studied only the action of their preparations on the photographic plate. By means of the electroscope it was now found that the uranium, even after the separation of the uranium X, showed almost undiminished activity, and it was proved in this way that only the β- and γ-rays belonged to the uranium X, but that the uranium itself emitted the whole of the α-rays. Rutherford and Soddy[4] further studied the time-rate of the decay of the radiation emitted by uranium X, which conformed exactly to the increase of the β- and γ-radiation emitted by the uranium which remained. It decays in geometrical progression with the time, so that the original activity is reduced to one-half in about twenty-two days, to one-fourth in forty-four days, and to one-eighth in sixty-six days. The curves (Fig. I.) illustrate the law according to which the decay, or the increase, as the case may be, of the radiation, took place. If the original activity of the β-radiation of the uranium is called I_0, the activity after the time t (in seconds) I_t, then we have the equation $\frac{I_t}{I_0} = e^{-\mu}$, in which e is the base of the natural log-

[1] Compt. rend., **133**, 977 (1901).
[2] J. Chem. Soc., **81**, 860 (1902).
[3] Phil. Mag. [6], **4**, 315 (1902).
[4] *Ibid.* [6], **5**, 422 (1903).

arithms and λ a constant, the so-called "radioactive constant." Its value amounts, in the foregoing case, to 3.6×10^{-7}, on an average. For the increase of the β-radiation of the uranium, the complementary equation $\frac{I_t}{I_0} = 1 - e^{-\lambda t}$ holds.

These facts can now be simply explained if we assume that the uranium is continuously giving up α-particles to form atoms of uranium X, which, on their part, undergo a further very rapid change with the loss of an electron. What the nature of this change may be, we can not for the present definitely say.

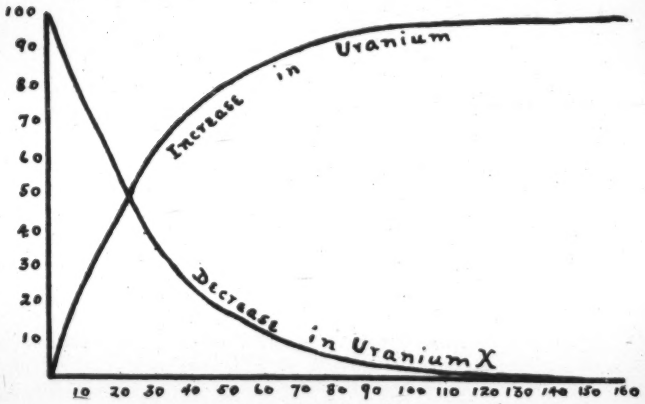


Fig. 1.

If the transformation of the uranium proceeds so slowly, in comparison with that of the uranium X, that the number of uranium atoms present does not appreciably alter during the period in which the atoms of uranium X, present at a given time, are completely changed into the next stage of their transformation, then it is evident that the uranium, after it has been separated from the uranium X, must again

produce in this period the same number of uranium X atoms, and therefore regain its original radiating power. It is then in a state of radioactive equilibrium with its products of decomposition.

The radiating power of a radioactive element is, according to this hypothesis, proportional to the number of atoms of it which are present. If one designates the number of atoms present at the beginning by N_0, the number present after the time t by N_t, then the above equation takes the usual form for a reaction of the first order: $N_t = N_0 \times e^{-\lambda t}$.

The radioactive constant gives the fraction of the atoms which are transformed in a second and its reciprocal, $1/\lambda$, is the average lifetime of an atom of the element in question. For uranium X this has a value of 32 days. The radioactive constant is independent of the temperature within the widest limits which are accessible to observation. It is often the only safe characteristic which we have for the rapidly changing radioactive substances, the so-called metabols. But just as little as we could doubt the existence of helium when it was only known by the Frauenhofer line of the element in the sun's spectrum, just so little do we doubt the reality and individuality of a metabol which is characterized only by its activity constant.

If the radiation of a radioactive substance does not proceed simultaneously from each of its atoms, but only from those which at the moment are breaking down, then according to the theory of probability the exponential law will be true only if the number of the atoms present can be assumed as infinitely great.[1] Otherwise the intensity of the radiation from a preparation will be subject to fluctuations. E. Meyer and Regner[2] recently confirmed this consequence of the hypothesis by measuring the saturation current produced by a feeble polonium preparation, while Regner[3] obtained similar results by counting the scintillations produced by it on a zinc blende screen.

[1] von Schweidler: Ueber Schwankungen der radioaktiven Umwandlungen, 1er Congrès Internat. Étude Radiologie et Ionization, Liège, 1905.

[2] Verh. d. physik. Ges., **10**, 1 (1908).

[3] *Loc. cit.*

VI. The Transformation Products of Thorium.

Even before they studied the radioactive transformation of uranium Rutherford and Soddy[1] had observed exactly similar relations for thorium, but as these relations are complicated, it seemed advisable to discuss the later investigations first. If thorium hydroxide is dissolved in an acid and reprecipitated by caustic soda it is obtained with unchanged radiating power, but if ammonium hydroxide is used, the activity of the precipitate is only 45 per cent that of the original. If the solution is evaporated and the ammonium salts driven off by ignition, an unweighable residue remains, the so-called thorium X, which possesses the remainder of the activity of the thorium. The change of radioactivity in this case occurs at first irregularly, for reasons which are now perfectly clear but the discussion of which shall be given later. The activity of the thorium diminishes on the first day and that of the thorium X increases correspondingly, but after this there occurs a regular increase of the activity of the thorium and a corresponding decrease of that of the thorium X according to an exponential law, so that after three weeks the activity of the former has regained its original value, while that of the latter has quite disappeared (Fig. II.). The life of thorium X is shorter than that of uranium X; the activity has fallen to half its value in 3.64 days.[2] This value is called its constant of half decay.

While the decomposition product of uranium X is not known, that of thorium X was discovered even before the separation of the latter from the mother element had been effected. It is the thorium emanation.[3] If air is allowed to pass over certain compounds of thorium, or through the solution of thorium salts, it carries with it a radioactive gas which is called the emanation. Its effects persist for only a very short time, the activity of the gas being reduced to one-half in 54 seconds. The gas diffuses slowly and therefore has a high density; it may

[1] J. Chem. Soc., **81**, 321, 837 (1902).
[2] von Lerch: Monats. Chem., **26**, 899 (1905).
[3] Owens: Phil. Mag. [5], **48**, 360 (1899). Rutherford: *Ibid.*, **49**, 1 (1900). Rutherford and Soddy: *Ibid.* [6], **4**, 569 (1902); **5**, 561 (1903).

be condensed at the temperature of liquid air and, like the noble gases, appears to be incapable of combination. The emanating power of thorium solutions is proportional to

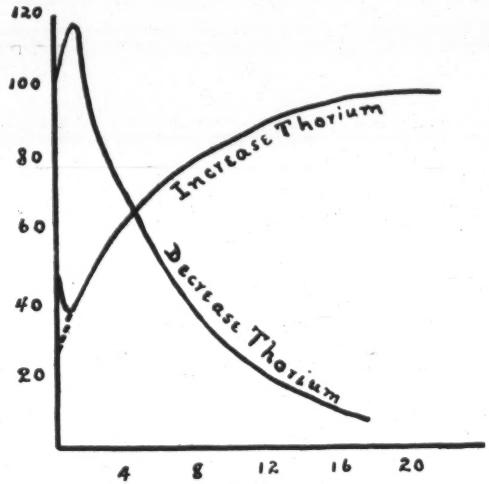


Fig. II.

their content of thorium; that of solid thorium compounds, on the other hand, varies greatly with the composition of the substances, because these occlude the emanation in varying degree. If, therefore, thorium X is separated from the solution of a thorium salt, the latter loses its power to produce emanation completely, but on the other hand the thorium X now gives off emanation very strongly. Consequently the emanation is a transformation product of thorium X.

Upon all surfaces with which the emanation comes into contact there is deposited a radioactive substance which is produced by the breaking down of the atoms of the emana-

tion. As early as 1899, P. and S. Curie[1] had observed that all objects which were placed in vessels containing radium salts became temporarily radioactive. This phenomenon they called "induced activity." Rutherford[2] noticed the occurrence of a similar phenomenon in the case of thorium and established its connection with the emanation. If the latter is allowed to pass over a negatively charged metal wire, the radioactive particles are deposited on it, while they do not collect on the wire if its charge is positive. The decomposition product of the emanation must therefore be positively charged. The particles, which are necessarily invisible and unweighable, can be rubbed off the wire mechanically, or be dissolved in mineral acids. If the acid solution is evaporated the radioactive constituent remains; the activity decays to half value with a constant of about 11 hours. In the solid thorium compound the emanation often remains occluded, as we saw above, and therefore the products of its decay must also collect in the solid. This explains why the activity of the thorium, after its separation from thorium X, at first continues to decrease, while that of the thorium X increases. The "induced activity" of the thorium remains in the thorium fraction, but decays practically completely in about one day, in which time it reaches its maximum in the thorium X, from which the emanation is being formed.

If the thorium emanation is allowed to act upon a surface only for a short time the activity given to the surface increases at first for several hours to a maximum and then begins to decrease with its normal period. Its behavior proves that the thorium activity so induced is not homogeneous, but that, on the contrary, from the first product of decay of the emanation a second is formed which is more strongly radioactive. Rutherford names these metabols thorium A and B. From the law of change of the activity of these he was able to deduce mathematically that one substance has a constant of half decay of 11 hours and the other of 45 minutes. Pe-

[1] Compt. rend., **129**, 714 (1899).
[2] *Loc. cit.* and Phil. Mag. [6], **5**, 95 (1903).

gram[1] and von Lerch[2] were able to separate partially thorium A and B because the latter is noticeably more noble than the former.

Miss Slater[3] effected a fairly complete separation by heating inside a lead case a platinum wire which had been charged with a mixture. At about 700° the thorium A began to sublime from the wire to the case; at 1000° almost pure thorium B remained on the wire, and it volatilized completely only at about 1200°. Recently Hahn[4] has shown that thorium B is not a simple substance for it gives out two kinds of α-rays. He assumes that it forms a thorium C with a very short period of decay of only a few seconds. The final product of the radioactive change of thorium is not known.

In sediments from springs in Baden-Baden, Elster and Geitel[5] found a constituent which gave off thorium emanation but did not contain a corresponding amount of thorium. The same observation has been made by Blanc[6] in the case of the sediment of other springs. Almost at the same time Hahn[7] separated from crude radium obtained from thorianite an impurity which resembled thorium completely in its chemical behavior, but was much more active than ordinary thorium. This he named radiothorium. The separation of this from thorium by chemical reagents has not yet been attained; only by producing certain precipitates in thorium solutions, for example, by precipitating iron hydroxide or barium sulphate, can a small fraction of the radiothorium be carried down.[8] Its time of half decay was found by Blanc[9] to be 737 days. Its short lifetime makes it very probable that radiothorium is an intermediate step between thorium and thorium X, and that such is the case is settled beyond doubt by the investigations of Boltwood, of Dadourian, and of McCoy

[1] Phys. Rev., **17**, 424 (1903).
[2] *Loc. cit.*
[3] Phil. Mag. [6], **9**, 628 (1905).
[4] Physik. Z., **7**, 412, 456 (1906).
[5] *Ibid.*, **6**, 67 (1905).
[6] Acc. Lincei [5], **15**, I., 328, 349 (1906).
[7] Chem. News, **92**, 251 (1905).
[8] Elster and Geitel: Physik. Z., **7**, 445 (1906). Blanc: Acc. Lincei [5], **15**, II., 90 (1906).
[9] Acc. Lincei [5], **16**, I., 291 (1907).

and Ross,[1] who found that the radioactivity of all thorium minerals is proportional to the thorium they contain.

It is altogether different, according to the same investigators, with the thorium compounds found in commerce. These all show a smaller activity than would be expected from the amount of the element present in them. The explanation of this fact, furnished by Hahn,[2] is that the thorium is not converted directly into radiothorium, but that an intermediate substance, mesothorium, which, in contradistinction to radiothorium, is removed in the separation of the thorium from the minerals, must be assumed to intervene. Mesothorium must have an appreciably longer lifetime than radiothorium because the thorium salts, after their separation from the ores, slowly lose activity, inasmuch as the radiothorium which they contain decays more rapidly than it is formed. The minimum appears to be reached in about three years and the constant of decay of mesothorium may be estimated roughly at seven years. It emits only β-rays, while the thorium which has been freed from radiothorium gives out α-rays. The following table gives the products of transformation of thorium:[3]

Name.	Time of half decay.	Kind of rays.
Thorium	$> 10^{10}$ years	α
↓		
Mesothorium	7 years (?)	β
↓		
Radiothorium	737 days	α
↓		
Thorium X	3.64 days	α
↓		
Emanation	54 seconds	α (δ)
↓		
Thorium A	10.6 seconds	β
↓		
Thorium B	55 minutes	α } β,γ
↓		
Thorium C	a few seconds (?)	α }

[1] Am. J. Sci. [4], **21**, 409, 427, 433 (1906).

[2] Ber. d. chem. Ges., **40**, 1462, 3304 (1907).

[3] Hahn [Physik. Z., **9**, 245 (1908)] has found recently that the β-rays of mesothorium are produced by a short-lived decomposition product, whose constant of half decay is 6.2 hours. He estimates the constant of half decay of the rayless mesothorium at 5.5 years.

VII. Transformations and Origin of Radium.

The discovery of the emanation from thorium was followed closely by that of radium emanation.[1] All solid radium compounds give out emanation only in very slight degree, but their solutions, on the other hand, emit it continuously. As this emanation has a much longer period of decay than the thorium emanation, requiring about 3.86 days to reach half value,[2] a considerable quantity of emanation thus collects in the solid substances and is suddenly set free on dissolving them, or it may also be driven out by heating the salts. On account of its comparatively long lifetime, it has been possible to study its properties thoroughly. Its velocity of diffusion has been determined many times,[3] and according to this its molecular weight would be less than 100, a value which is probably much too low; owing to the enormously great dilution at which it was determined, it is very uncertain. The gas is inert and therefore probably composed of single atoms; it may be condensed in liquid air[4] and evaporates at $-150°$. Ramsay and Collie[5] have investigated its spectrum and found certain relations to the gases of the argon group. The radium emanation emits α-rays and also δ-rays.[6]

The induced activity deposited by this emanation decays almost completely in a few hours. In dry radium salts which have been kept for a considerable time, the radium is in radioactive equilibrium with the occluded emanation and the products of its decay. If the salt is dissolved, and the solution is evaporated, the emanation is given off. The residue at first still contains these products of decay, whose radiation very rapidly dies down, and in consequence the activity of the salt at first decreases, but in a few hours reaches a minimum, at which point it is equal to only a quarter of that of the "ripened" salt, and after this increases in the course of a month

[1] Dorn: Abh. Naturf. Ges., Halle, **1900**.

[2] Sackur: Ber. d. chem. Ges., **38**, 1753 (1905).

[3] Rutherford and Brooks: Phil. Mag. [6], **4**, 1 (1902). Curie and Danne: Compt. rend., **136**, 1314 (1903). Makower: Phil. Mag. [6], **9**, 56 (1905).

[4] Rutherford and Soddy: Phil. Mag. [6], **5**, 561 (1903).

[5] Compt. rend., **138**, 1388 (1904).

[6] Slater: Phil. Mag. [6], **10**, 460 (1905).

to its original value. In the same time the emanation set free completely decomposes, although in the first hours after its separation its radiating power increases as the products of its decay increase. As the quantities of energy concerned in the case of these substances are great, Rutherford and Barnes[1] were able to follow this behavior by means of the calorimeter. As we saw before, 1 gram of radium gives out more than 100 calories in an hour, three-fourths of which large amount of energy must be ascribed to the unweighable quantities of the products of its decay existing in radioactive equilibrium with it.

Ramsay and his collaborators[2] have tried to measure the quantity of emanation produced by radium, but the values which they obtained agree so poorly among themselves and with those of other observers that these investigations are in need of confirmation. The emanation given off in 3.86 days from 1 gram of radium amounts to 1 cubic mm., according to the older experiments, and to 3.5 cubic mm., according to the later measurements. In the latter case there was observed a contraction, which is as yet unexplained, of the emanation to half its value in the course of an hour after its isolation.

The decay of radium emanation gives rise to "induced" activity, which, as in the case of thorium, consists of a series of metabols arising one from another, only in this case the series is much longer. We have said that the induced activity of radium decays very rapidly, but this is not strictly correct, as there remains at last a small residue whose activity does not noticeably decrease. This we will leave out of consideration for the present. The activity of a wire which has been exposed for several hours to the action of radium emanation decreases according to a law which may be expressed as the difference of two exponential functions, but if the action of the emanation has lasted only a few minutes the induced activity decreases at first with a constant of half

[1] Phil. Mag. [6], **7**, 202 (1904).

[2] Ramsay and Soddy: P. Roy. Soc., **73**, 346 (1904). Ramsay and Cameron: Jahrb. Radioakt., **4**, 253 (1907).

decay of 3 minutes, and after this in a very complicated manner.[1] Rutherford[2] has explained this phenomenon on the basis of the disintegration hypothesis as follows: At first there is formed from the emanation a metabol called radium A which decays with a period of 3 minutes. This emits α-rays and is changed into radium B which gives out no rays, and this in turn into radium C which gives out α-, β-, and γ-rays. The constants of half decay of radium B and radium C, for which he at first assumed incorrect values, were determined by Bronson[3] to be 26 and 19 minutes, respectively. H. W. Schmidt[4] then showed that radium B possesses a slow β-radiation, and lastly von Lerch[5] succeeded in separating electrolytically radium C from a solution of the induced activity acidified with hydrochloric acid. From this solution, free from radium C, he was able to carry down the radium B by a precipitate of barium sulphate. The rays from radium C are especially interesting because it is the only element of the radium series which produces γ-rays and it gives out its α-rays with a greater velocity than any other substance known up to this time. They can penetrate 7 cm. of air at normal pressure, while the α-rays from radium itself can traverse only half that distance.

The induced activity of radium vanishes almost entirely in the course of a day, but there remains then a very slight activity which was first observed by S. Curie.[6] Rutherford[7] has studied thoroughly this "residual activity." It shows α- and β-radiation, but neither kind of rays decreases; on the contrary, both increase and, curiously enough, according to different exponential laws, until finally they become almost constant. Rutherford explains this phenomenon by the assumption that radium C is transformed into a metabol, radium D, which gives out no rays and has a very long life-

[1] P. Curie and Danne: Compt. rend., **136**, 364 (1903); **138**, 683, 748 (1904).
[2] Trans. Roy. Soc., **204**, A, 169 (1904).
[3] Am. J. Sci. [4], **20**, 55 (1905).
[4] Physik. Z., **6**, 897 (1905).
[5] Sitzun. Wien., **115**, IIa, 197 (1906).
[6] Ann. chim. phys. [7], **30**, 289 (1903).
[7] Phil. Mag. [6], **8**, 636 (1904); **10**, 290 (1905).

time, and is transformed into radium E, which gives out β-rays. Finally, this decays, with the formation of radium F, which gives out α-rays. The time of half decay of radium D was found to be, very roughly, 40 years, that of radium E, 6 days, that of radium F, 143 days.

The lifetime of radium D could be determined only indirectly by comparison of the β-rays which are given out by the radium C and radium E from the same amount of emanation. By a similar calculation based upon the α-rays given out by radium C and radium F, St. Meyer and von Schweidler found a very different constant of half decay, 25 years.

That radium E is changed into radium F was proved by Rutherford. If the residual activity is heated to 1000° the radium F volatilizes, together with the greater part of the radium D, but radium E, which produces all the β-rays, and also the rest of the radium D remains. But radium F, which gives out α-rays, again begins to be formed and, in fact, in consequence of the short period of decay of radium E, it is formed very rapidly at first, but later on, when the radium E is largely consumed, it is formed more slowly, in proportion as the radium D already present is transformed into radium E. The radium E which remains as a residue from the heating shows a smaller constant of decay than would be given by the increase of the β-rays from the residual activity, namely, 4.5 days. This fact has been explained by St. Meyer and von Schweidler.[1] They showed that radium F is electrochemically more negative than radium E, which in turn is more negative than radium D. By electrolysis of acid solutions of the residual activity at a suitable potential difference the individual metabols can be separated from one another. In this way it is found that a precipitate giving off β-rays with a period of half decay of 4.8 days follows the radium F and is, in turn, followed by a rayless form with a period of about 6 days. As the former is formed from the latter they are named by these authors radium E_1 and radium E_2.

The most important result of Rutherford's investigations on the residual activity was the proof that radium F is iden-

[1] Lieben-Festschrift, 402 (1906).

tical with polonium. S. Curie[1] has already shown that the activity of polonium is not constant, but the decrease which she noticed was irregular, evidently because her preparation was very impure. When polonium was separated from other substances by the above-described process it was found to decay exponentially. The period of this decay has been determined many times and the most reliable observations give the constant for half decay as 139–140 days. Rutherford found, as we saw above, 143 days for radium F, St. Meyer and von Schweidler[2] 138 days, which is in satisfactory agreement with the former. The identity of the two substances is also further established by their electrochemical behavior.

Radium D is found in the lead fraction in the analytical separation of uranium ores. As it does not itself give out rays, the radioactivity of the lead obtained from the ore depends upon the transformation products of the radium D. The "radioblei" of K. A. Hofmann and Straus[3] is therefore a mixture of lead with residual activity. So far, no one has succeeded in separating radium D from lead, but Hofmann and Wölff[4] effected a certain amount of enrichment of the chloride by fractional sublimation and also still better by transforming the lead into its tetraphenyl compound.

Along with the above radioactive transformation products there is found another substance, the occurrence of which is of the greatest interest. This is helium. Rutherford considers it probable, as we saw, that the α-particles are helium atoms, and Ramsay and Soddy[5] have proved that the radium emanation, as a matter of fact, forms helium as it breaks down. This observation has been repeatedly confirmed by other observers[6] under the most various conditions of experiment. Special mention must be made of an investiga-

[1] *Loc. cit.*

[2] St. Meyer and von Schweidler: Sitzun. Wien, **114,** IIa, 389, 1195 (1905); **115,** IIa, 63 (1906). Marckwald, Greinacher, and Hermann: Jahrb. Radioakt., **2,** 136 (1905). S. Curie: Physik. Z., **7,** 146, 180 (1906).

[3] Ber. d. chem. Ges., **33,** 3570 (1900).

[4] *Ibid.*, **40,** 2425 (1907); Ann. Phys. [4], **15,** 621 (1904).

[5] P. Roy. Soc., **72,** 204 (1903).

[6] Curie and Dewar: Compt. rend., **138,** 190 (1904). Indrikson: Physik. Z., **5,** 214 (1904). Himstedt and Meyer: Ann. Phys. [4], **15,** 184 (1904). Giesel: Ber. d. chem. Ges., **38,** 2300 (1905); **39,** 2244 (1906).

tion by Himstedt and Meyer[1] which was completely free from the objection that the helium might have been occluded in the radium salts and have escaped with the emanation, as the radium bromide was repeatedly distilled and the formation of helium in this salt after several weeks was then proved. Remembering in this connection that all uranium ores contain helium in large quantity, we should find in these facts an important confirmation of Rutherford's hypothesis as to the nature of the α-particles, were it not for the fact that recent investigations throw a certain doubt upon this view. Ramsay and Cameron[2] have caused the decomposition of the radium emanation to take place, not, as in former experiments, by itself, but in presence of water and of copper solutions. There was then found no trace of helium but, instead, neon in the former and argon in the latter case. In the copper solutions there was formed at the same time lithium, which could be recognized by its spectrum, and probably sodium also. These most astonishing observations require, however, further study, which has already been begun by the authors with larger quantities of radium. The outcome is looked forward to with the greatest expectation.

If radium decomposes regularly into α-particles and emanation it must be possible to calculate its period of decay, which is too long to be measured directly, by determining that of one or other of its decomposition products. Now, as we have seen, the quantitative estimation of the amount of emanation from a given amount of radium is very uncertain. On the other hand, the intensity of the α-radiation may be measured with the electrometer with considerable accuracy. Assuming that each particle carried only one charge, Rutherford[3] found that the total number of α-particles given off by 1 gram of pure radium, freed from its products of decay, in 1 second was 6.2×10^{10}, but on the more probable assumption that the α-particles are helium atoms with two electric charges this value must be halved. If we further assume that each atom,

[1] Ann. Phys. [4]. **17,** 1005 (1905).
[2] J. Chem. Soc., **91,** 1593 (1907).
[3] Phil. Mag. [6], **10,** 193 (1905).

on breaking down, gives out only one α-particle, then in 1 gram of radium 3.1×10^{10} atoms break up in unit time. Now, as is well known, the number of atoms of a substance contained in the atomic weight in grams may be taken to be 8×10^{23}. As the atomic weight of radium is 226, 1 gram of radium contains 3.6×10^{21} atoms. The fraction of these which decomposes in 1 second accordingly amounts to $3.1 \times 10^{10} \div 3.6 \times 10^{21} = 8.6 \times 10^{-12}$. This number, therefore, gives the radioactive constant of radium, from which it may be concluded that radium is half transformed in 2600 years. The accuracy of this speculation could be controlled by weighing. It is true that a radium salt, when kept in the dry state, would show only a negligible loss of weight inasmuch as the emanation formed would decompose, without escaping, into the nonvolatile metabols; on the other hand, a radium salt which was entirely unaffected by ignition—and such a substance is probably to be found in the sulphate—would lose 1/4000 of its weight in a year.

If, then, the period of decay of radium is very small in comparison with the intervals of time with which geology is accustomed to reckon, it is still clear that this element must owe its existence in pitchblende to the much slower transformation of some other original radioactive element. The only one in question here is uranium. Consequently radium and its products of decay must be in radioactive equilibrium with this in the uranium ores. This conclusion from the disintegration hypothesis has been confirmed in the most brilliant manner by recent investigations. McCoy[1] showed that the radioactivity of all uranium ores is approximately proportional to their uranium content, but 5 to 6 times as great as the activity of the uranium that they contain. While this made it probable that the radium and uranium in these ores existed in constant proportions, this fact was established exactly by the investigations of Boltwood[2] and Strutt[3] who measured gravimetrically the amount of uranium, and de-

[1] Ber. d. chem. Ges., **37**, 2641 (1904).
[2] Phil. Mag. [6], **9**, 599 (1905).
[3] P. Roy. Soc., **76**, 88 (1905).

termined the amount of radium by dissolving the ores, collecting the emanation, and measuring its activity with the electrometer. The proportion of uranium to radium agreed very closely in the case of most widely varying ores. Eve[1] came to the same conclusion by taking the very penetrating γ-rays of radium C as the measure of the radium contained in the uranium ores; and lastly Rutherford and Boltwood[2] determined the absolute proportion of the weight of radium to uranium in the ore in the case of a sample of pitchblende by comparing its emanating power with that of a radium solution obtained from it. They found the value 3.8×10^{-7}.

By means of this number we are now able to estimate the decay period of uranium, for if 1 gram of uranium is in equilibrium with 3.8×10^{-7} grams of radium and the constant of half decay of radium is 2600 years, then uranium must decay to half its value in $\frac{2600 \times 10^7}{3.8}$, that is, in 6.8×10^9 years. If this decomposition led directly to radium it ought to be easy to prove the presence of this element, for since 1 gram of uranium is in equilibrium with 3.8×10^{-7} grams of radium and the radioactive constant of radium is 8.6×10^{-12}, then 1 gram of uranium would form $8.6 \times 10^{-12} \times 3.8 \times 10^{-7}$ grams of radium in a second, that is to say, almost exactly 10^{-10} grams in a year. The amount of radium formed from 100 grams of uranium in a few weeks would be sufficient to make it possible to detect the presence of radium emanation with the electroscope. Boltwood[3] has begun experiments in this direction but has not been able to find a trace of emanation in the course of a year, although by the method he used he should have been able to detect the presence of as little as 1/1000 of the theoretical amount, and he concludes that between the short-lived uranium X, the first product of transformation of uranium, and radium, there exists at least one intermediate substance with a long lifetime.

This assumption has recently been verified in a surprising

[1] Am. J. Sci. [4], **22**, 4 (1906).
[2] *Ibid.* [4], **22**, 1 (1906).
[3] Am. J. Sci. [4], **20**, 239 (1905).

manner. No one would have supposed that in the uranium ores which have been so zealously studied for 100 years, there could be any other radioactive substance with appreciable radiating power which had escaped discovery. Through a remarkable coincidence such a substance has been discovered almost simultaneously by several experimenters. The first announcement was published by Boltwood,[1] who gave the element the name ionium. He found it, as did also Marckwald and Keetman,[2] in a great number of uranium ores. Ionium is very closely allied chemically to thorium. It gives out α- and β-rays, the former of which are characterized by an unusually small power of penetration, their range of action in air being less than 3 cm. As it appears to have a long lifetime it ought to be contained in considerable quantity in pitchblende. Its proportion to radium in various ores appears to be sensibly constant. Hahn[3] has discovered ionium as an impurity in commercial preparations of thorium. Its most interesting property, established independently by Boltwood and Hahn, is that it produces radium The freshly precipitated preparation, for example, gives out no emanation, if we disregard a slight trace of thorium emanation, but even after a few weeks the appearance of radium emanation can be demonstrated.

The decay period of uranium amounts to many thousand million years, consequently we feel hardly any greater necessity to answer the question as to whence this element comes, than to solve the riddle of the universe itself. We are much more concerned with the question as to what are the final products of the radioactive transformation process. Polonium with its short period of decay must evidently change into a more stable element. On the ground of hypotheses which are very uncertain, however, Rutherford has assumed that polonium decomposes into helium and lead. The atomic weight of radium is 226, and as each atom of radium and four of its products of decay, that is, polonium, the emana-

[1] Am. J. Sci. [4], **24**, 370 (1907).
[2] Ber. d. chem. Ges., **41**, 49 (1908).
[3] *Ibid.*, **40**, 4415 (1907).

tion, radium A, and radium C, give out an α-particle when they decompose, then, assuming that the α-particles are helium atoms, each product of transformation which gives out α-rays must decrease in atomic weight by that of helium, *i.e.*, by 4, and the product of decay of polonium should thus have an atomic weight of about 206 [226 — (5×4)], a value which is sufficiently close to that of lead, 206.9. The atomic weight of polonium would then be about 211, which, as we saw, would agree perfectly with its position in the periodic system, based on purely chemical grounds. These speculations found support in experiments of Boltwood's[1] on the amount of lead contained in uranium ores. He showed that not only do all uranium minerals contain lead and helium, but also that the amount of lead in such ores as, on geological grounds, must be assumed to be of the same age, is in a fixed proportion to their content of uranium, as the transformation hypothesis requires. That the same is not true of helium is no objection, since this would remain occluded to a greater or less degree according to the character of the ore.

From the decay period of uranium and the amount of lead in its ores we can, on this hypothesis, estimate the age of the ore. The primary minerals investigated by Boltwood have an age of from 400 to 2200 million years. Such minerals as gummite and uranophane, which are formed secondarily from pitchblende by external influences, can, of course, give no evidence of their age by the amount of lead they contain, but even these all contain lead. Recently, however, Marckwald and Keetman[2] have found that in 10 grams of autunite there is certainly less than 1/10 mg. of lead, if indeed it is present at all. If Rutherford's hypothesis is correct we should have to assume that the time since the deposition of the autunite in the locality in which it was found has not been long enough for the formation of noticeable quantities of lead. In other respects the activity of the autunite is

[1] Am. J. Sci. [4], **23**, 77 (1907).
[2] *Loc. cit.*

quite normal, so that uranium and radium exist in it in radioactive equilibrium.

Rutherford's hypothesis that lead is the final product of the radioactive transformation depends upon two assumptions, namely, that the α-particles consist of helium and that radium and only four of its metabols produce α-rays when they decompose. Since the latest observations of Ramsay and Cameron, this first assumption is, as we saw, no longer so certain as it previously appeared to be, when Ramsay and Soddy had proved the formation of helium from the emanation. To this we may add the fact that Greinacher and Kernbaum[1] tried in vain to establish experimentally the formation of this gas from polonium. Upon the second of Rutherford's assumptions, that only 4 metabols of radium give out α-rays, doubt has also been cast by Rutherford himself. Since the α-rays can only be demonstrated when their velocity is greater than 1/36 that of light, and since the maximum velocity of the α-particles, as in the case of radium C, is only 1/13, and their minimum velocity, as in the case of ionium, less than 1/20 of that of light, it is easy to imagine that even the so-called rayless metabols like radium D may emit slow rays. These might have half the velocity of the ionium rays without betraying their presence by causing ionization or by acting on the photographic plate. Calorimetrically, however, it ought to be possible to show their presence, if radium D were available in concentrated form. If such a slow radiation were assumed for these metabols their further transformation could be explained in the simplest way.

The question whether polonium can be transformed into lead is quite accessible to a direct experimental test. The amount of polonium obtainable from a year's output of the Joachimsthal mines should be enough for the determination of this important question. In the following table are given the transformation products of uranium with their most important characteristics:

[1] Physik. Z., 8, 339 (1907).

Name.	Time of half decay.	Kind of rays.
Uranium	6.8×10^9 years	α
↓		
Uranium X	22 days	β,γ
↓		
Ionium	?	α,β
↓		
Radium	2600 years	α (δ)
↓		
Emanation	3.8 days	α (δ)
↓		
Radium A	3 minutes	α
↓		
Radium B	26 minutes	β
↓		
Radium C	19 minutes	α,β,γ
↓		
Radium D	40(?) years	—
↓		
Radium E_1	6 days	—
↓		
Radium E_2	4.8 days	β
↓		
Polonium	140 days	α (δ)
↓		
Lead (?)	—	—

VIII. Actinium.

We have so far left out of account one of the radioactive constituents of pitchblende which was discovered by Debierne[1] shortly after the discovery of polonium and radium. He found it among the rare earths which are contained in small quantities in the mineral and gave it the name actinium. This substance is especially characterized by the fact that it gives out an emanation of very short lifetime. Later Giesel[2] came across actinium in the investigation of the earths which had accumulated in the mother liquors

[1] Compt. rend., **129**, 593 (1899); **130**, 906 (1900); **131**, 333 (1900); **136**, 446, 671 (1903); **138**, 411 (1904); **139**, 538 (1904); **141**, 383 (1905).

[2] Ber. d. chem. Ges., **35**, 3608 (1902); **36**, 342 (1903); **37**, 1696, 3963 (1904); **38**, 775 (1905); **40**, 3011 (1907).

of radium bromide. Here the substance was found concentrated to a considerable extent and was named emanium, on account of its high emanating power, before its identity with actinium had been established. Giesel showed that actinium was similar to lanthanum in chemical properties but that it could be partially separated from the latter by fractional crystallization of the double nitrate with manganese. However, the separation has so far been effected only in a very imperfect manner, as in the spectrum of the product the lanthanum line alone was found. The decay period of actinium appears to be very large since it has not been possible thus far to demonstrate any decrease in its activity.

The decay period of the actinium emanation is the shortest so far observed for any radioactive substance, having a constant of half decay of 3.9 seconds, consequently the action of relatively small quantities of this emanation is exceptionally great. It can be condensed at a temperature above that of liquid air,[1] like other emanations, and emits only α-rays. It is also very striking that it is attracted by negatively charged electrodes, that is to say, it is itself charged positively like the "induced activity." This positive charge is probably likewise due to the occurrence of δ-rays. Like the radium emanation it decomposes with the formation of helium.

The induced activity of actinium decreases to half its value in about 36 minutes. Rutherford[2] and Brooks[3] showed that when the emanation acts only for a short time it forms a very feebly active deposit, whose activity rises rapidly to a maximum and then steadily falls off. The case is therefore similar to that of thorium and must be explained by assuming the formation of a rayless metabol, actinium A, from which actinium B is produced. The latter gives off α-, β-, and γ-rays. By careful study[4] of the progress of this change in activity it is found that the two metabols decay with constants of

[1] Goldstein: Verh. d. physik. Ges., **5**, 392 (1903).
[2] Trans. Roy. Soc., **204**, A, 169 (1904).
[3] Phil. Mag. [6], **8**, 373 (1904).
[4] Bronson: Am. J. Sci. [4], **19**, 185 (1905). Meyer and von Schweidler: Sitzun. Wien., **114**, IIa, 1147 (1905).

36 and 2 minutes, respectively. Actinium B is more electronegative than actinium A and may therefore be separated from the latter by electrolysis of the hydrochloric acid solution of the active precipitate. By this means it was established that actinium B has the shorter decay period of the two. Levin[1] separated the two metabols by taking advantage of their difference in volatility. Actinium A volatilizes slowly at as low a temperature as 400°, while actinium B does not escape below 700°. Meyer and von Schweidler[2] believe that by long action of the actinium emanation they have obtained evidence of a further "residual activity" whose period of half decay is 12 days, but they themselves consider the existence of actinium C as uncertain.

The change of the actinium into emanation does not occur directly, but there are two intermediate metabols. That which is produced directly from the emanation was discovered first and designated as actinium X. It is separated just like thorium X, by precipitating the actinium from its solution by means of ammonia. The precipitate is found to be devoid of emanating power. The minute quantity of residue that remains after the evaporation of the solution and after the ammonium salts have been driven off by ignition is strongly active and gives out emanation strongly. Its activity decreases with a constant of 10.2 days, while that of the ammonia precipitate increases at the same rate.[3]

The actinium which has been freed from actinium X still gives out α-rays, but if thiosulphate is added to this solution there is precipitated along with the sulphur an unweighable quantity of a substance which produces the whole of the α-radiation, and the actinium hydroxide then precipitated from the solution by ammonia is quite inactive. Hahn,[4] who established this fact, named the constituent precipitated by thiosulphate radioactinium. This substance has no power of emanating immediately after it is precipitated, but acquires the same, reaching a maximum in the course of several

[1] Physik. Z., **7**, 812 (1906).
[2] Wien. Akad. Anz., **12** (Apr. 26, 1906).
[3] Godlewski: Phil. Mag. [6], **10**, 35 (1905). Levin: *Loc. cit.*
[4] Ber. d. chem. Ges., **39**, 1605 (1906); Physik. Z., **7**, 855 (1906).

weeks, after which the activity begins to decay, decreasing to half value in 19.5 days. The radiating power of the actinium increases at the same rate. These observations prove that the actinium itself is rayless, but decomposes into radioactinium, and this further forms actinium X. We obtain in this manner the following pedigree for the decay products of actinium:

Name.	Time of half decay.	Kind of rays.
Actinium	?	—
↓		
Radioactinium	19.5 days	α
↓		
Actinium X	10.2 days	α
↓		
Emanation	3.9 seconds	α
↓		
Actinium A	36 minutes	—
↓		
Actinium B	2.15 minutes	α,β,γ
↓		
Actinium C (?)	12 days (?)	(?)

Of the total activity of pitchblende, that of actinium and its decay products forms only a small fraction, consequently the question whether it occurs in all uranium ores and whether it is present in these in a constant proportion to the uranium they contain, is still undecided.[1] If the latter were proved to be true it would be necessary to assume a connection between the radioactive transformation of uranium and the formation of actinium. On the other hand, the rayless actinium may also possess a lifetime comparable in magnitude to that of uranium and thorium and would thus represent a third original radioactive element.

IX. The Radioactivity of the Atmosphere, the Earth, and Springs.

That a charged electroscope gradually loses its charge

[1] In a paper which has just appeared [Am. J. Sci. [4], **25**, 269 (1908)] Boltwood makes some very interesting contributions to this question and to that of the radioactivity of uranium ores in general, but unfortunately they appeared too late to be considered.

in the air has long been known, but it was not until the year 1900 that Geitel[1] and Wilson[2] independently proved that this discharge must be attributed chiefly to the ions in the air. The observation that the discharging power of a closed volume of air at first increases, as must be the case, owing to the formation of induced activity, in a gas containing radium emanation, led Elster and Geitel[3] to undertake in the following year the classical experiment to determine whether the decay products of this emanation existed in the air. For this purpose they set up a wire of considerable length in the open air and charged it for many hours to a high negative potential. It was then found as a matter of fact to possess a noticeable activity which showed all the properties of induced radioactivity and especially the characteristic decay period.[4] If a wire is exposed for many days to the induction it is found that after the induced activity from radium has disappeared, there still remains a residue which decays with the slower period of the induced activity of thorium.[5] The amount of radioactive substances in the atmospheric air depends upon the locality and upon meteorological conditions. To account for the emanation contained in the air Elster and Geitel[6] assumed the existence of radium in the earth and confirmed this assumption, in the first place, by showing that the air in cellars, caves, and the interstices of the earth is much more strongly ionized than in the atmosphere. The carbon dioxide from springs that arise from great depths, like the helium[7] from the Tuscan fumaroles, contains considerable quantities of radium emanation.

Investigation of the earth's crust shows that as a matter of fact it possesses in all cases traces of permanent radioactivity. Clay soils,[8] as contrasted with more compact rocks, are characterized by a greater activity due to the presence of

[1] Physik. Z., **2**, 116 (1900).
[2] P. Camb. Phil. Soc., **11**, 32 (1900).
[3] Physik. Z., **2**, 590 (1901).
[4] Rutherford and Allen: Phil. Mag. [6], **24**, 704 (1902).
[5] Bumstead: Am. J. Sci. [4], **18**, 1 (1904).
[6] Physik. Z., **3**, 574 (1902); **4**, 522 (1903).
[7] Nasini, Anderlini, and Levi: Acc. Lincei [5], **14**, II., 70 (1905).
[8] Elster and Geitel: Physik. Z., **5**, 11, 321 (1904).

radium. Many volcanic rocks are much richer still in radium. Soil from near Capri showed about 1/1000 of the activity of pitchblende and the "fango" which is deposited by the hot springs of Battaglia is about equal to it in activity. From each of these Geitel[1] was able to obtain some radium mixed with barium.

The waters of springs carry off the emanation accumulated in the pores of the earth and give it up to the air according to Dalton's law.[2] Petroleum takes up the emanation in even greater quantity.[3] Many springs coming from great depths are especially rich in the radium emanation and consequently many thermal and medicinal springs have been thoroughly investigated with reference to their content of radioactive substances. The springs of Germany have been especially investigated by Himstedt, Henrich, Engler and Sieveking, H. W. Schmidt, Hinrichsen and Sahlbom; those of Austria by Mache; of England, by Allan and by Strutt; of France, by P. Curie and Laborde; of Spain, by Muñoz de Castillo; of Italy, by Nisini, Blanc and Engler; of Russia, by Sokolow; and of America, by Boltwood. Most of these springs contain only radium emanations, but some contain dissolved radium and a few thorium emanations also. For the investigation of these springs many pieces of apparatus have been described which make possible a certain and rapid determination of their activity. The most used of these is the "fontactoscope" of Engler and Sieveking.[4]

When thermal springs contain dissolved radium it is often deposited along with the slime or sinter near the point at which they rise. Like the "fango" which was mentioned above, the sediments of the springs at Nauheim, Kreuznach, and Baden-Baden are very rich in radium. These deposits sometimes contain in addition radiothorium (see above).

Although the radioactivity of many medicinal springs is

[1] Ber. d. chem. Ges., **38,** 132 (1904).

[2] Sella and Pochettino: Acc. Lincei [5], **11,** I., 527 (1902). J. J. Thomson: Phil. Mag. [6], **4,** 352 (1902). Adams: Phil. Mag. [6], **6,** 563 (1903). Himstedt: Physik. Z., **4,** 482 (1903); **5,** 210 (1904). Ann. Phys. [4], **13,** 573 (1904).

[3] Himstedt: *Loc. cit.* Burton: Physik. Z., **5,** 511 (1904).

[4] Physik. Z., **6,** 700 (1905).

certainly of no consequence with regard to their therapeutic value, it appears that in certain cases their specific principles depend upon the emanation they contain. It is known, for instance, that the hot springs of Gastein are almost free from dissolved salts, but surpass almost all known medicinal springs in the amount of emanation they contain. Now it has been shown experimentally by Loewenthal[1] that an aqueous solution of radium emanation which has no noticeable action on healthy people produces in chronically rheumatic invalids all those phenomena which are known as the "bath-reactions."

Sea water also contains radium.[2] According to Joly's[3] latest measurements the radium contained in 1 cubic meter of sea water amounts on the average to 1.7×10^{-5} mg.

X. The Heat-budget of the Earth.

The recognition of the wide-spread occurrence of radium in the earth makes it possible to explain a contradiction between the views of geologists and physicists in regard to the age of the crust of the earth. While geologists feel obliged to estimate the age of the earth's crust at least at 1000 million years, Lord Kelvin calculated a minimum value of 40 million years from the temperature of solidification, the geothermal gradient, and the heat capacity of the earth's surface. As we saw above, Boltwood's calculated values for the age of the uranium ores come close to the estimates of the geologists. If these are correct, there must be a continual production of heat in the earth, which has been overlooked in the calculations of the physicists. Such a source of heat is found in radium. Rutherford[4] has calculated how much radium must be contained in 1 cc. of earth to keep the temperature of the earth constant. This would require an evolution of heat amounting to 2.2×10^{-7} cal. yearly. Then, as 1 gram of radium evolves in a year more than 876,000 cal., the presence of 2.6×10^{-13} grams of radium

[1] Physik. Z., **7**, 563 (1906).
[2] Strutt: P. Roy. Soc., A, **78**, 151 (1906). Eve: Phil. Mag. [6], **13**, 248 (1907).
[3] Phil. Mag. [6], **15**, 385 (1908).
[4] Die Wissenschaft, **21**, 213 (1907).

in 1 cc. of earth would be sufficient to make up for its loss of heat by radiation. Now it has been shown by Strutt[1] in numerous investigations of the most commonly occurring rocks that the crust of the earth contains on the average about 8×10^{-12} grams radium, that is to say, about 30 times as much as the amount calculated by Rutherford to be necessary to keep the temperature of the earth constant. If we remember, moreover, that the heat evolved by uranium, thorium, io.ium, and actinium has been left out of account, we see that there cannot possibly be as much radioactive substance decomposing in the interior of the earth as in the crust; otherwise the temperature of the earth would rise instead of sinking. Perhaps this contradiction may be explained by supposing that under the enormous pressure and at the high temperature of the interior of the earth the radioactive processes proceed more slowly or even in an opposite direction.[2]

XI. The Energy Content of the Atoms.

The radioactive decomposition of actinium emanation is 5×10^{16} times faster than that of uranium. It is therefore natural to suppose that there are radioactive substances whose lifetime surpasses that of uranium many million times. The radiation from such substances would escape detection by the electrometer. Campbell[3] and others believe that they have noticed in many metals, particularly in lead, a slight radioactivity which, it must be admitted, is barely beyond the limits of experimental error. Together with Wood,[4] he has lately announced that potassium salts show a relatively considerable β-radiation, but it is very difficult, in consequence of the widespread occurrence of radium, to prove with certainty that every trace of this and of its decay products has been excluded. Elster and Geitel[5] invariably found a slight activity in commercial lead compounds, but they were able to separate polo-

[1] P. Roy. Soc., **77, A**, 472 (1906).
[2] Lewin: Z. Elek. Chem., **27**, 390 (1907).
[3] Phil. Mag. [6], **9**, 531 (1905); **11**, 206 (1906). P. Camb. Phil. Soc., **13**, 282 (1906)
[4] P. Camb. Phil. Soc., **14**, 15, 211 (1907).
[5] Physik. Z., **7**, 841 (1906); **8**, 273, 776 (1907).

nium from them. They therefore supposed that radium D, which is closely allied to lead, is the cause of the common activity of this metal. This supposition was confirmed when they established the fact that samples of lead of great age, in which the radium D which might have been originally present would have decayed, possessed no activity.

H. Greinacher[1] has investigated the question as to whether activity may be detected in ordinary substances by means of the calorimeter. The result was negative.

It is therefore by no means proved experimentally that radioactivity is a universal property of matter, but on theoretical grounds we cannot escape the conception that no difference in principle can be assumed between the radioactive elements and other elements with regard to their energy content. One gram of radium in radioactive equilibrium with its rapidly decaying metabols evolves, as we saw, about 120 cal. an hour. If we take the average lifetime of the radium atom as 3700 years, the change of 1 gram of radium as far as radium D will set free $3700 \times 8760 \times 120$ cal. $= 389 \times 10^4$ cal., *i. e.*, as much heat as would be evolved by the combustion of 500 kilograms of coal. This amount of energy, however, is plainly only a small fraction of that which remains latent in the residual atoms.

We know of no means of accelerating the decomposition of radioactive atoms. If we had such a means we would probably be in a position to transform other elements with its help. In this way we might expect to be able to form other elementary substances of smaller atomic weights, with a simultaneous gain of enormous quantities of energy. If the change occurred suddenly it would be accompanied by the most frightful explosions, but if on the other hand we were able to regulate it at will, then we certainly could obtain from 1 kilogram of pitchblende, and perhaps even from the same weight of lead, enough energy to carry a great express steamer over the Atlantic ocean.

It was the dream of the alchemists to transform the baser into the noble metals. The radioactive substances have

[1] Ann. Phys. [4], **24**, 79 (1907).

taught us that if this process were successful there would either be obtained thereby so much energy that in comparison with it the value of the noble metal produced would be of little account, or on the contrary the energy required in turning the metal into a more noble one would be so great as to make the process perfectly valueless.

However, we do not need to wander in the realms of fancy in order to find important and valuable questions concerning radioactivity which remain yet to be solved. Chemical investigation has not kept pace here with physical investigation. This can be easily understood, because chemical investigations require a greater outlay for material and are therefore very costly. In this matter the words of Martial will certainly prove to be true: "Sint Maecenates, non deerunt, Flacce, Marones." (Give us a Maecenas (*i. e.*, a rich patron), and the Virgil will not be wanting, Horace.)

REVIEWS.

THERMODYNAMICS OF TECHNICAL GAS REACTIONS. By DR. F. HABER, Professor at the Technische Hochschule, Karlsruhe. Translated by ARTHUR B. LAMB, PH.D. Longmans, Green, & Co. 1908. pp. xix + 356.

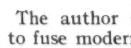
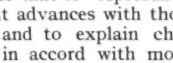
The object of this book is well stated both in the preface of the author and in that of the translator. It is a most important contribution to the general problems of thermodynamics, and has special reference to the possibility of predicting the course and extent of chemical reactions from a knowledge of a few characteristic constants of the substances taking part in the reaction. The work is based upon the theoretical papers of Helmholtz and is largely the logical development of the former's theoretical formulae. The book is divided into seven lectures, as follows: The first lecture discusses the latent heat of chemical reaction and its relation to reaction energy. This is practically a summary of the elementary theory of thermodynamics. The second lecture discusses entropy and its significance in gas reactions. This chapter contains the derivation of Helmholtz's formula and gives several interesting illustrations and applications. In the third lecture there is another derivation of the formula previously obtained and a discussion of its bearing on relations between solids; in an appendix is given Nernst's addition

to the theory. The fourth lecture contains illustrations of certain reactions, such as the formation of nitric oxide, of hydrobromic acid, the water-gas reaction, etc. In the fifth lecture there are illustrations of other reactions, involving a change in the number of molecules, such as the formation of carbon dioxide, of water, of sulphuric acid, etc. The sixth lecture contains a description of the experimental methods for the determination of the specific heats of gases; and the seventh lecture discusses gaseous equilibrium and other allied subjects.

In no other text book is there such a complete treatment of the applications of thermodynamics to chemical phenomena, nor such a successful attempt to extend the theory to all classes of phenomena and to bring the data down to the most recent investigations. J. S. AMES.

A TEXT-BOOK OF EXPERIMENTAL CHEMISTRY (with Descriptive Notes) for Students of General Inorganic Chemistry. By EDWIN LEE, Professor of Chemistry in Allegheny College. Philadelphia: P. Blakiston's Sons & Co. pp. 433. Price, $1.50.

This book is written for beginners. The author says in the preface that it "represents an effort to fuse modern views and recent advances with those older views which have stood the test, and to explain chemical phenomena in a manner which is in accord with modern chemical thought." Other recent writers have made the same effort, some with notable success.

It seems to the reviewer that Professor Lee offers too much theoretical matter and much of this too early. Two examples are offered. Chapter VII. is called "Outlines" and is intended for the teacher, not for the student; it contains a synopsis of lecture topics and *precedes* oxygen, which is the first element treated. The synopsis of formulae is as follows: "Empirical, Ex., H_2O, $C_2H_4O_2$. Rational, Ex., $HC_2H_3O_2$. Dualistic, Ex., H_2O,SO_3. Na_2O,SO_3. Na_2O, H_2O. Typical, $\left.\begin{matrix}H\\Cl\end{matrix}\right\}$, $\left.\begin{matrix}H\\H\end{matrix}\right\}$O, $\left.\begin{matrix}H\\H\\H\end{matrix}\right\}$N. Structural or graphic,  , , Na—OH,  . Space (formulae of more than one dimension to represent the configuration of molecule.)" Dualistic and typical formulae belong to past history and are only of interest if we know *how* and *why* they were introduced. Is this a fit subject for lectures to beginners?

A chapter on solutions follows the chapters on oxygen,

hydrogen, and water. Two pages are given to surface and diffusion phenomena and to solution tension; of this a half page is filled by an abstract of a recent article by Hulett in the *Journal of the American Chemical Society*, followed by a paragraph of comment on Hulett's work quoted from Morgan. The next experiment is on osmotic pressure, with two pages of description of the work of Pfeffer and of that of Morse and Frazer on cane sugar, giving the tabulated results of the work of the latter chemists at 20° with concentrations from 0.05 to 1 00 mole per liter. Is this fit matter for a text book for beginners? Compare this with the cautious and gradual introduction of physical-chemical theory in Ostwald's "Grundlinien," in Holleman's "Inorganic Chemistry," and in Alexander Smith's "General Chemistry" and laboratory manual.

Professor Lee's book is written with an enthusiasm and love for the subject which, if helped by his own teaching, would inspire his students, but it seems to the reviewer that a thorough revision of the book is necessary to make it a success.

E. R.

A TEXT-BOOK OF INORGANIC CHEMISTRY. By DR. A. F. HOLLEMAN, Professor Ordinarius in the University of Amsterdam; Emeritus Professor Ordinarius in the University of Groningen, Netherlands, and Fellow of the Royal Academy of Sciences, Amsterdam. Issued in English in coöperation with HERMAN CHARLES COOPER. Third English edition, partly rewritten. New York: John Wiley & Sons; London: Chapman & Hall, Limited. 1908. pp. 502.

The appearance of the first edition of this book was noticed in THIS JOURNAL by the present reviewer[1]. Attention was also called to the appearance of the English translation.[2] We all welcome the quick appearance of the third edition of this work in English. "The present edition represents a thorough revision of the work by both the Dutch author and the American editor. The portions on the phase rule, spectroscopy, radioactivity, iron-carbon system, and metal-ammonia compounds have seen largely rewritten by the author, and the chapter on colloids, experimental determination of equivalent weights, and unity of matter, are entirely new."

The above quotation from the preface gives some idea of the nature of the revision to which the book has been subjected. The reviewer will have to differ with the translator when he says that "Notwithstanding the appearance of differential formulae in the book, it is believed that a student who is unfamiliar with the calculus should have little difficulty

[1] THIS JOURNAL, **27**, 159.
[2] *Ibid.*, **28**, 241.

in understanding the meaning and use of such formulae, provided he is willing to take the author's word for the solutions of the equations."

May the book find as large a sale as it merits. H. C. J.

CENTENARY OF THE PUBLICATION OF AVOGADRO'S MEMOIR ON THE MOLECULAR CONSTITUTION OF GASES.

On the initiative of the Royal Academy of Sciences of Turin, a committee has been organized to provide a suitable memorial to Amedeo Avogadro to mark the 100th anniversary of the appearance of his epoch-making paper on the molecular constitution of gases, which was published in 1811. It appears to the committee that there can be no more fitting way to honor the memory of this great chemist and physicist than by the publication of a volume containing his chief works and by the erection of a monument at Turin, his birthplace and the scene of his labors.

Appeal is therefore made to all chemists and physicists in the hope that they will make it possible, by their contributions, to pay this tardy but well-merited tribute to a man as great as he was modest and to whom science owes so much. The editor of THIS JOURNAL will be pleased to receive all such contributions and forward them to the Treasurer of the Royal Academy, Via Maria Vittoria, 3, Turin.

Sen. Enrico Canizzarro is honorary president of the committee, which consists of an executive committee composed of members of the Turin Royal Academy, and a promotion committee including the presidents of the various Italian Royal Academies, Institutes, and Physical and Chemical Societies, the presidents of the London, Paris, Berlin, St. Petersburg and American Chemical Societies, the president of the Geneva Société de Physique, and a number of prominent chemists and physicists of Europe and America. The American members are named below: F. W. Clarke, W. W. Coblentz, A. Michael, A. A. Michelson, E. W. Morley, J. U. Nef, A. A. Noyes, W. H. Nichols, I. Remsen, T. W. Richards.